

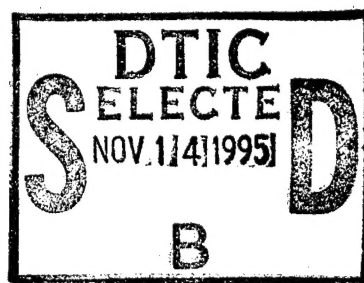
# NIOSH



## RESEARCH REPORT

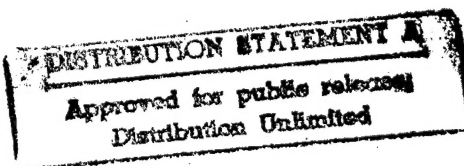
### Engineering Control Technology Assessment for the Plastics and Resins Industry

19951108 202



PLASTED 38749

DEPARTMENT OF DEFENSE  
PLASTICS TECHNICAL EVALUATION CENTER  
ARRADEON, ROYER, M. J. 07001



DTIC QUALITY INSPECTED 6

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
Public Health Service  
Center for Disease Control  
National Institute for Occupational Safety and Health

not in NTFS  
RST  
4/15/01

\*MSG DI4 DROLS PROCESSING - LAST INPUT IGNORED

-- 2 OF 2

-- \*\*\*DTIC DOES NOT HAVE THIS ITEM\*\*\*

-- 1 - AD NUMBER: D432250  
-- 5 - CORPORATE AUTHOR: ENVIRO CONTROL INC ROCKVILLE MD  
-- 6 - UNCLASSIFIED TITLE: ENGINEERING CONTROL TECHNOLOGY ASSESSMENT  
-- FOR THE PLASTICS AND RESINS INDUSTRY,  
--10 - PERSONAL AUTHORS: BOCHINSKI, J. H. ;  
--11 - REPORT DATE: MAR , 1978  
--12 - PAGINATION: 242P  
--14 - REPORT NUMBER: DHEW/PUB/NIOSH-78/159  
--15 - CONTRACT NUMBER: PHS210-76-0122  
--20 - REPORT CLASSIFICATION: UNCLASSIFIED  
--22 - LIMITATIONS (ALPHA): APPROVED FOR PUBLIC RELEASE; DISTRIBUTION  
-- UNLIMITED. ~~AVAILABILITY: DIV. OF TECHNICAL SERVICES, PUBLICATIONS,~~  
-- ~~NIOSH ROBERT A. TAFT LABS., 4676 COLUMBIA PARKWAY, CINCINNATI, OH.~~  
-- ~~45226~~  
--33 - LIMITATION CODES: 1

-- END

Y FOR NEXT ACCESSION

END

ENGINEERING CONTROL TECHNOLOGY ASSESSMENT  
FOR THE PLASTICS AND RESINS INDUSTRY

Enviro Control, Inc.  
Rockville, Maryland 20852

Contract No. 210-76-0122

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
Public Health Service  
Center for Disease Control  
National Institute for Occupational Safety and Health  
Division of Physical Sciences and Engineering  
Cincinnati, Ohio 45226

March 1978

#### DISCLAIMER

The contents of this report are reproduced herein as received from the contractor, except for minor editorial changes.

The opinions, findings, and conclusions expressed herein are not necessarily those of the National Institute for Occupational Safety and Health, nor does mention of company names or products constitute endorsement by the National Institute for Occupational Safety and Health.

NIOSH Project Officer: James A. Gideon  
Principal Investigator: Julius H. Bochinski



**DHEW (NIOSH) Publication No. 78-159**



# ABSTRACT

A control technology assessment for the plastics and resins industry was made by conducting in-depth surveys of 15 polymerization and compounding processes. The processes selected provide a representative coverage of the industry relative to the number of exposed workers, different control techniques and commonality of operations. Case study summaries presented for each of the sites surveyed included:

- Major toxic chemicals and harmful physical stresses
- Engineering controls and work practices
- Workplace monitoring systems and air sampling programs
- Personal protection equipment
- Exposure data and conclusions
- Planned or ongoing improvements

The results of this study are useable as a reference resource by both industry and government personnel. A number of problem areas in systems analysis, mechanical engineering design, research and testing, and ventilation control are identified as likely candidates for research and development by the National Institute for Occupational Safety and Health (NIOSH) and industry.

<b>Accession For</b>	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification <i>per printout and loose</i>	
By <i>DTIC AI memo 2 Nov 95</i>	
Distribution/	
<b>Availability Codes</b>	
<b>Dist</b>	Avail and/or Special
<i>A-1</i>	

## CONTENTS

Disclaimer.....	ii
Abstract.....	iii
Acknowledgments.....	viii
Introduction.....	1
Industry Overview.....	4
Research Recommendations.....	10
Summary and Conclusions.....	15
User Guide and Subject Indices.....	17
Index I.    Plastic or Resin Product.....	18
Index II.   Manufacturing Process.....	19
Index III.  Toxic Chemical or Harmful Physical Agent.....	20
Index IV.   Control Techniques.....	22
Appendixes	
A.1.  PVC Mass Polymerization Process - Case Study No. 1.....	30
A.2.  PVC Mass Polymerization Process - Case Study No. 2.....	45
A.3.  PVC Suspension Process - Case Study No. 3.....	60
A.4.  PVC Dispersion Polymerization Process - Case Study No. 4.....	71
A.5.  PVC Dispersion and Suspension Procedures - Case Study No. 5.....	86
A.6.  ABS-SAN Resin Manufacture - Case Study No. 6.....	100
A.7.  Polystyrene Process - Case Study No. 7.....	114
A.8.  Styrene Butadiene Rubber Emulsion Polymerization Process - Case Study No. 8.....	120
A.9.  Phenolic Resin Production - Case Study No. 9.....	129
A.10. Alkyl Phenol Resin Production - Case Study No. 10.....	134
A.11. Liquid and Solid Epoxy Process - Case Study No. 11.....	144
A.12. Toluene Diisocyanate Process - Case Study No. 12.....	159
A.13. Phenolic Resin Compounding Process - Case Study No. 13.....	165
A.14. A General Description of Compounding Controls.....	179
A.15. Monitoring Instrument System Employing a Fourier Intere- ferometer.....	184
A.16. Monitoring Instrument System Employing a Gas Chromatograph Sensor.....	197
B.     General Flow Charts and Process Descriptions.....	200
C.     Process Description for Compounding Operations.....	214
D.     Health Effects.....	219
Glossary.....	228
References.....	232

## FIGURES

Figure 1.  Integration of Plastics and Resins Industry: Scope of Study.....	6
---	---

Figure A.1-1.	Polyvinyl Chloride Plant Bulk Process Flow Sheet.....	31
Figure A.1-2.	Bulk Process Reactor.....	33
Figure A.1-3.	General Ventilation.....	39
Figure A.1-4.	Monthly Gas Chromatograph Data Averages.....	41
Figure A.1-5.	Steam-Water Mixer.....	43
Figure A.2-1.	PVC Mass Polymerization Process Flow Sheet.....	46
Figure A.2-2.	Vent Compress System (Wharton Compressor).....	52
Figure A.2-3.	Local Exhaust System.....	54
Figure A.2-4.	General Ventilation System.....	55
Figure A.3-1.	PVC Suspension Process.....	61
Figure A.3-2.	Waste Water Vapor Containment System.....	63
Figure A.3-3.	Local Exhaust System for Reactor Floor Area (TOP VIEW).	66
Figure A.3-4.	Average Personal Sampling Results.....	69
Figure A.4-1.	PVC Dispersion Polymerization Process Flow Diagram.....	72
Figure A.4-2.	Employee Exposure by Job Function.....	82
Figure A.4-3.	Average Area VCM Concentration at Work Stations.....	83
Figure A.5-1.	PVC Suspension Process Flow Sheet.....	87
Figure A.5-2.	PVC Dispersion Process.....	88
Figure A.5-3.	General Ventilation System.....	96
Figure A.6-1.	Block Diagram - ABS Plastics Manufacturing Process.....	101
Figure A.6-2.	ABS Plastic Manufacturing Process.....	102
Figure A.6-3.	Top View of Floc Pot.....	106
Figure A.6-4.	Sectional View A-A of Floc Pots shown in Figure A.6-3..	107
Figure A.7-1.	Polystyrene Process Flow Sheet.....	115
Figure A.7-2.	Area Noise Levels - Process Area.....	118
Figure A.8-1.	Copolymer Plant Flow Sheet - Polymerization Area.....	121
Figure A.8-2.	Copolymer Plant Flow Sheet - Process Area.....	122
Figure A.9-1.	Novolak Process for Phenolic Resins.....	130
Figure A.10-1.	Alkyl Phenol Resin Process.....	135
Figure A.10-2.	Mixing Tank Vent Scrubber System.....	139
Figure A.11-1.	Liquid and Solid Epoxy Resin Processes.....	145
Figure A.11-2.	Fail Safe Pumping System.....	146
Figure A.11-3.	Specifications for Control Interlock System.....	147
Figure A.11-4.	Splash Cover for Vertical In-Line Pump - General Specification.....	148
Figure A.11-5.	Splash Cover for Refinery Type Centrifugal Pump - General Specification.....	149
Figure A.11-6.	Typical Hardpiped Drain for Process Equipment Containing Hazardous Material.....	150
Figure A.11-7.	Filter Backwash System.....	152
Figure A.11-8.	Off-Spec Recycle Filter Decontamination System and Associated Instruments.....	154
Figure A.11-9.	Catalyst Vacuum Loader.....	155
Figure A.11-10.	Truck and Tank Car Loading Arms.....	156
Figure A.12-1.	TDI Process Flow Sheet.....	160
Figure A.13-1.	Phenolic Resin Process Flow.....	166
Figure A.13-2.	Local Ventilation System.....	171
Figure A.13-3.	Ribbon Mixer Charge Booth.....	173
Figure A.13-4.	Discharge Hood.....	174
Figure A.13-5.	Rolls Hood.....	175
Figure A.13-6.	Rework Hopper.....	176
Figure A.15-1.	Block Diagram - VCM Monitoring System.....	185

Figure A.15-2.	Plot Plan Upper Level - Plant #1.....	186
Figure A.15-3.	Plot Plan Lower Level - Plant #1.....	187
Figure A.15-4.	Location of Test Probes - Six-Point System - Upper Level - Plant #1.....	189
Figure A.15-5.	Probability of an Excursion Above 25 ppm - Upper Level - Plant #1.....	190
Figure A.15-6.	Probability of a Man in an Area. (Results of Time and Motion Study).....	191
Figure A.15-7.	Sample Transport System.....	192
Figure A.15-8.	Observed Airborne VCM for a Fixed Point in the Plant...	195
Figure A.15-9.	Employee VCM Exposure for Typical Work Month.....	196
Figure A.16-1.	Instrument Monitoring System Employing a Process Gas Chromatograph - Block Diagram.....	198
Figure C-1.	Compounding Process Flow Diagram.....	215

## TABLES

Table 1.	Resin vs. Output and Exposed Workers.....	5
Table 2.	Processes and Products of the Plastics and Resins Industry .....	8
Table 3.	Resin vs Manufacturing Process.....	9
Table A.1-1.	Seals for Compressors, Pumps and Agitators.....	36
Table A.2-1.	Seals for Compressors, Pumps and Agitators.....	53
Table A.2-2.	Comparison of Employee Exposure Data*.....	57
Table A.5-1.	Seals for Compressors, Pumps and Agitators.....	92
Table A.6-1.	Seals for Pumps, Agitators, Valves and Flanges.....	104
Table A.6-2.	Area Sampling Data.....	108
Table A.6-3.	Area Sampling Data - Flocculation Building.....	109
Table A.6-4.	Personal Sampling Data.....	109
Table A.6-5.	Summary of Acrylonitrile Data - August 1977.....	110
Table A.6-6.	Personal Sample Data for Selected Tasks.....	111
Table A.6-7.	Noise Survey Results - Flocculation Building.....	113
Table A.7-1.	Seals for Pumps and Valves.....	116
Table A.7-2.	Personal and Area Samples for Styrene.....	117
Table A.10-1.	Air Sample Data.....	142

## ACKNOWLEDGMENTS

The Division of Physical Sciences and Engineering, National Institute for Occupational Safety and Health, supported this engineering control technology assessment for the plastics and resins industry. James A. Gideon (Project Officer) participated in this study and worked closely with Kenneth S. Schoultz and Julius H. Bochinski in the evolution of this report. The division management staff who provided guidance for this study included Robert Hughes and John Talty.

The interest of the plastics and resins industry and the technical input of the staffs assigned to cooperate with the investigators made a study of this type possible.

The views expressed and conclusions reached in this document are the result of careful review of the information obtained during site visits, a search of the published literature and consideration of comments from external reviewers.

## INTRODUCTION

A major segment of the research and development efforts of the National Institute for Occupational Safety and Health (NIOSH) is directed toward the publication of an ongoing series of criteria documents that present recommended standards for permissible employee exposures to potentially harmful chemical or physical agents in the workplace. The NIOSH documents are designed to provide information for industrial health and safety programs, as well as for technical and research bases of activities of the Occupational Safety and Health Administration (OSHA).

Experience has indicated that merely stating safe conditions for occupational exposure to potentially harmful materials in the workplace is incomplete without some consideration of how these standards can be achieved.

In order to answer the questions of how a given safe exposure condition in the workplace can best be achieved, NIOSH has initiated a control technology program. The initial portion of the program involves a series of industry-wide engineering control\* technology assessments, designed to document and evaluate effective control technology options for the processes found in each industry, and to outline control technology research needs. The follow-up phase will entail effective dissemination of the program results to aid industry in voluntarily applying pioneered and implementable control technology options.

The plastics and synthetic resins industry, including the manufacture and compounding of thermoplastics and thermosetting resins and synthetic rubber (SIC Codes 2821 and 2822), was the choice for the first assessment. The contract to perform this assessment was awarded to Enviro Control, Inc. (ECI) in July 1976. The results of the work performed under this contract are presented in this report.

The report is organized to provide the reader with a convenient means for locating the information of interest:

- "Industry Overview" -- identifies the processes used, products produced, and number of workers involved in the manufacture of each of the major products. The scope of this study is also defined.
- "Research Recommendations" -- sets priorities and describes areas where

---

\*Engineering controls are defined as any measure taken to control employee exposure, by inhalation or skin contact, to toxic chemical agents or harmful physical stresses. Such control measures can range from actual changes in the processes and equipment to implementation of safer work procedures.

research and development are needed in order that the needs of both industry and workers will be met.

- "Summary and Conclusions" -- summarizes the state of the industry and supports what directions future research on worker exposure should take.
- "Users Guide and Subject Indices" -- identifies the potentially hazardous situations found during this study and lists both the engineering controls observed by the investigators and those reported in the literature.
- "Appendix A" -- presents results of site visits in terms of 15 detailed case studies, so that users can determine whether specific engineering controls described would meet their needs.
- "Appendix B" -- includes general flowcharts and process descriptions to provide the users with a broader background of the processes involved in the plastics and resins industry.
- "Appendix C" -- presents description of the processes generally used for compounding operations in the plastics and resins industry.
- "Appendix D" -- presents brief summaries of the adverse health effects associated with each of the major raw materials, as well as any existing Federal exposure limits.

In-plant studies of engineering control technology were completed for 15 polymerization and compounding processes. Each case study involves a distinct polymerization process and evaluates the techniques used to reduce or eliminate employee exposure to toxic chemical agents and harmful physical stresses. The processes selected provide a representative coverage of the industry relative to the number of exposed workers, different control techniques and commonality of operations. The individual case studies include summaries of the processes and evaluations of the following:

- Major toxic chemicals and harmful physical stresses
- Engineering controls and work practices
- Workplace monitoring systems and air sampling programs
- Personal protection equipment
- Exposure data and conclusions
- Planned or ongoing improvements

The selection of plants to be surveyed was governed by the following considerations:

- A disproportionate number of PVC processes was selected for study because of the high toxicity of vinyl chloride and the promulgation of the OSHA standard which resulted in the existence of numerous effective engineering control systems. The most advanced control technology available in the

industry is contained in these plants and is largely applicable to other plastics and resin processes and, to a lesser extent, other chemical processes.

- Although processes for manufacturing polyethylene and polypropylene employ a large number of workers and comprise a large percentage of total plastics and resin production, they were not selected for study because of the low toxicity of input materials and the concomitant improbability of their implementing many useful control techniques.
- There is a readily apparent difference between the extent of engineering controls in the PVC processes, the TDI process, and the epoxy process, and the extent in other polymerization processes. In the former three processes, exposure to materials used is tightly regulated, as even low concentrations may cause gross acute effects. Such rigorous control is imperative. In the latter processes, materials used are not so tightly regulated, and thus the process characteristics (i.e., closed process) alone can provide sufficient containment of process toxicants.
- Only one compounding process is included (Case Study 13, Phenolic Resin Compounding). Six other compounding processes were observed and either they did not possess state-of-the-art controls, or potentially effective controls were provided, but not sufficiently maintained for proper containment. Since dust control in compounding operations appears to be a problem, a general critical evaluation describing the shortcomings of observed operations follows the final case study.

This study is intended for use by the public and private sectors:

- NIOSH should use the information in planning and guiding research and development of engineering control technology.
- Industry should find the information useful in selecting engineering controls for hazardous work areas in identical or similar situations. Also, equipment manufacturers could use the information supplied in identifying markets for improved and new products or services.
- The OSHA staff could use the information primarily for training field personnel and provide them with a better understanding of the problems. This report is not designed to legally support the promulgation of control technology across industrial segments.
- Industrial hygienists could use the study as a reference when advising plant personnel and their representatives on the availability and effectiveness of engineering controls.



## INDUSTRY OVERVIEW

For the purpose of this study, the Plastics and Resins Industry is defined as those processes used to manufacture the polymerized materials listed in Standard Industrial Classification (SIC) Codes 2821 and 2822 (Table 1). The plastics and resins industry is unique relative to the chemical industry, i.e., reactions cause high viscosity products, usually two phases are formed, processes usually cannot be closed, large quantities of heat must be removed, etc. The scope of the study is depicted in Figure 1. It does not include the manufacture of any raw material, either from the Basic Petrochemical Industry, the Industrial Organic Chemical Industry or the Plasticizer Industry. It also does not include any downstream operation including the Synthetic Fiber Industry, the Fabrication Industry or the Coatings and Adhesives Industry where plastics or resins products are turned into marketable commercial products. The study does include compounding operations where various additives are utilized with the plastic or resin material to impart desirable qualities for future use.

Under SIC Code 2821, Plastics Materials, Synthetic Resins and Non-Vulcanizable Elastomers, there are two broad classifications: Thermoplastic Resins which are produced by addition polymerization processes, and Thermosetting Resins which are made by condensation polymerization processes. The thermoplastic resins may be remolded with the addition of heat and the thermosetting resins may not be. SIC Code 2822 includes the synthetic rubbers, which are generally manufactured using additional polymerization processes similar to those used for thermoplastic resins.

Table 1 presents the 1974 production figures for the major plastics, resins and synthetic rubbers. Also included is an estimate of the number of exposed workers in the manufacture of each of the major products. As shown, 15 plastics and resins in SIC Code 2821 comprise over 90% of the yearly production in the industry. Similarly, 7 major synthetic rubber products in SIC Code 2822 yielded over 95% of yearly production.

The numbers of exposed workers indicated for each product are rough estimates. Actual figures are impossible to obtain because of the amount of integration within the industry. In other words, a plant may produce a PVC resin, but also have facilities to produce the feedstock materials, and to convert the PVC resin into a fabricated product. The support staff such as maintenance, utilities, etc. would be common to all these facilities. Since a large percentage of exposed workers in this industry is made up of support staff, it is impossible to break out accurate figures of exposed workers in the process of interest. Further, since most available manufacturing census data are on total employees (many who would not be considered exposed), the task of estimating exposed workers becomes more complicated. However, for the purpose of this study, the estimates provided in Table 1 are considered adequate.

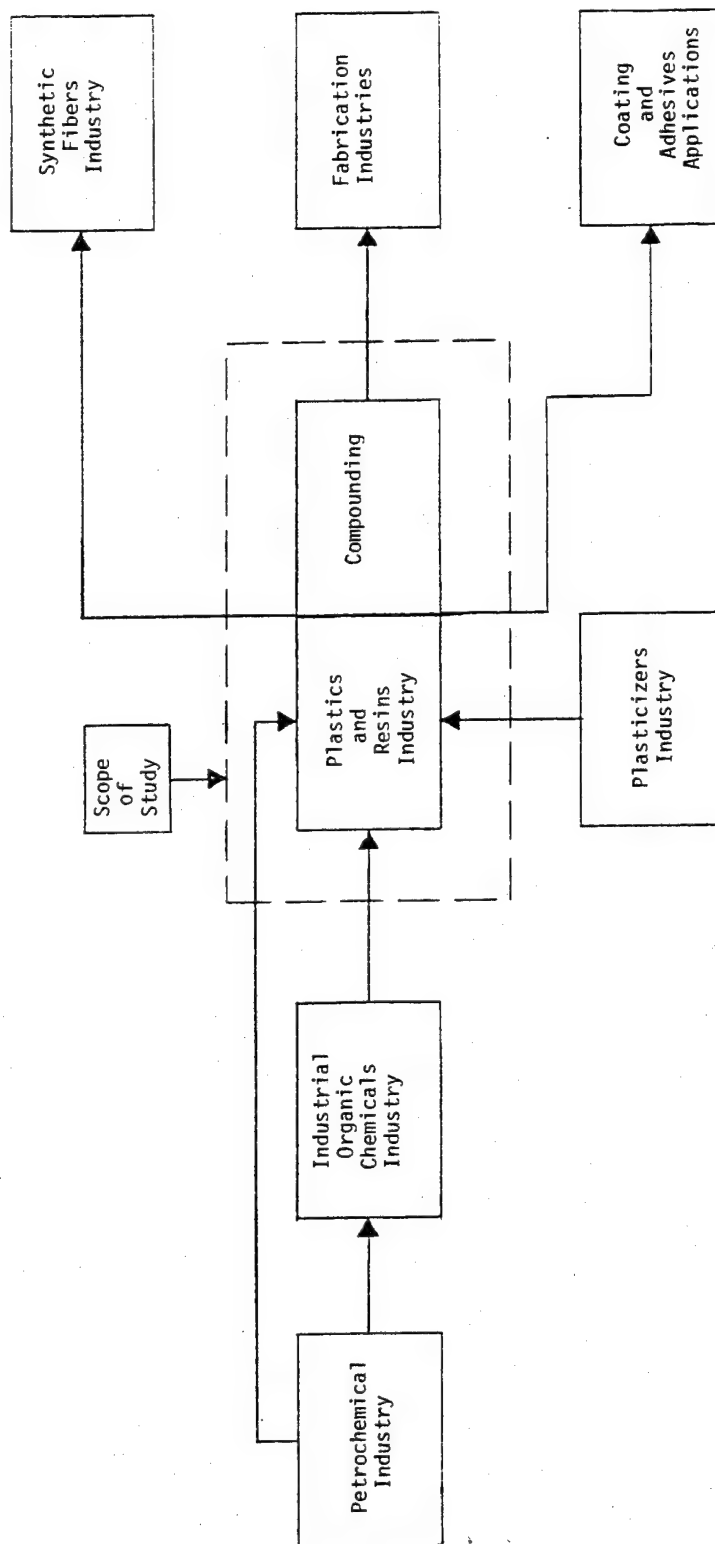
Table 1. Resin vs. Output and Exposed Workers

SIC 2821 -- Plastic Materials, Synthetic Resins and Nonvulcanizable Elastomers			
Resin	1974 Production <sup>1</sup> (1,000,000 lbs)	Percent of Total Production	Exposed Workers <sup>2</sup>
Acrylonitrile-Butadiene-Styrene/ Styrene-Acrylonitrile	751	2.5	780
Acrylic	1180	3.9	1184
Alkyd	693	2.3	750
Aminoplasts (melamine and urea-formaldehyde)	1235	4.1	1230
Coumarone-Indene and Hydrocarbon	407	1.3	340
Epoxy (saturated and unsaturated)	312	1.0	260
Phenol	1340	4.4	1670
Polyamide	320	1.1	175
Polyester	1071	3.5	1260
Polyethylene (total) (high density) (low density)	8845 2745 6100	29.2	7900
Polystyrene	3130	10.3	3030
Polypropylene	1900	6.3	1860
Polyurethane	1520	5.0	1900
Polyvinyl Acetate	540	1.8	680
Polyvinyl Alcohol	140	0.5	150
Polyvinyl Chloride and Copolymers	4200	13.9	4040
All Other	1931	8.9	2336
Total	30251	100.0	29,545
SIC 2822 -- Synthetic Rubbers			
Rubber	1974 Production <sup>1</sup> (1,000,000 lbs)	Percent of Total Production	Exposed Workers <sup>3</sup>
Butyl	360	6.7	460
Ethylene Propylene	280	5.2	375
Neoprene	360	6.7	500
Nitrile	200	3.7	275
Polybutadiene	710	13.3	895
Polyisoprene	190	3.6	280
Styrene-Butadiene	3000	56.1	3950
All Other	250	4.7	330
Total	5350	100.0	7065

<sup>1</sup>Sources: U.S. International Trade Commission, *Synthetic Organic Chemicals*, U.S. Production and Sales; Society for the Plastics Industries

<sup>2</sup>Based on extrapolation from estimates in *Economic Analysis of Proposed Effluent Guidelines, The Plastics and Synthetic Industry*, Phase 1 (unpublished), and from data obtained during plant surveys.

<sup>3</sup>Based on extrapolation from employment data in the 1972 Census of Manufactures (MC 72(2)-288), and from data obtained during plant surveys.



*Industrial Process Profiles For Environmental Use: Chapter 10; Plastics and Resins Industry;*  
 Industrial Environmental Research Laboratory, Office of Research and Development, U.S. Environmental  
 Protection Agency, Cincinnati, Ohio

Figure 1. Integration of Plastics and Resins Industry: Scope of Study

The commercial polymerization processes can be divided into the 20 categories listed in Table 2. The operating parameters and equipment design within a process category may vary widely for each of the products produced within the category. General production flow charts and process descriptions are provided for each of the process categories in Appendix B.

The most common manufacturing processes for the thermoplastic resins and synthetic rubbers are mass (or bulk), suspension, emulsion and solution-precipitation addition polymerization. As illustrated in Table 3, most of the resins and rubbers are manufactured using more than one (or all) of these processes, depending on the specific plant and the end use of the resin. The thermosetting resins are manufactured using a condensation polymerization process; these are listed separately in Table 3.

Compounding operations are difficult to categorize as to production figures or numbers of exposed workers. Compounding operations are found at the polymerization plant, at small specialty compounding plants, or at any of the downstream industries, including synthetic fibers, resin fabrication, and coatings and adhesives. Only those compounding plants located at polymerization plants were surveyed during the course of the study. General flow charts and process descriptions for compounding operations are presented in Appendix C.

Table 2. Processes and Products of the Plastics and Resins Industry\*

PROCESS	PRODUCTS	PROCESS	PRODUCTS
Mass Addition Polymerization	Polystyrene Acrylonitrile-Butadiene-Styrene Styrene-Acrylonitrile Methyl Methacrylate Allyl Resins Polyvinyl Chloride Latices Polystyrene Acrylonitrile-Butadiene-Styrene Styrene-Acrylonitrile Polyvinyl Chloride Polyvinyl Acetate Polyvinylidene Chloride Polyalkyl Acrylates and Copolymers Polyalkyl Methacrylates and Copolymers Polyvinyl Esters and Copolymers Polyacrylonitrile Polybutadiene Polychloroprene Polyisoprene $\alpha$ -Methyl Styrene Copolymers Isobutylene Copolymers Styrene Butadiene Rubber Butyl Rubber	High Pressure Mass Polymerization Solution Polymerization	Low Density Polyethylene Styrene Polymers and Copolymers $\alpha$ -Methyl Styrene Copolymers Polyacrylic Acid Polymethacrylic Acid Polyacrylamide Polyvinyl Pyrrolidone and Copolymers Ethylene Propylene Neoprene Nitrile Rubbers Polybutadiene Polyisoprene Polyethylene Ethylene-Olefin Copolymers High Density Polyethylene Polypropylene Polybutene Various Copolymers
Emulsion Addition Polymerization	Solids Polyvinyl Chloride Plastisol Resins Styrene-Acrylonitrile Graft Polyblends with Synthetic Rubbers Teflon (polytetrafluoroethylene) Kel-F (polytrifluoroethylene) Polymethacrylic Esters and Copolymers Polyacrylic Esters and Copolymers Rubber-Modified Polystyrene Polyvinylidene Chloride (vinyl chloride copolymers) Polyvinyl Chloride and Copolymers Polyvinyl Acetate Styrene Acrylonitrile Rubber-Modified Styrene-Acrylonitrile Copolymers (i.e., ABS and others) Polydivinyl Benzene and Copolymers Polytrifluoroethylene	Particle Form Polymerization (polyethylene) Polyolefins Polymerization (Ziegler)  Phenolic Resin Production Amino Resin Production Polycarbonate Production Epoxy Resin Production Unsaturated Polyester Resin Production  Alkyd Resin Production Polyethylene Terephthalate Production Nylon 6 Production Nylon 66 Production Polyurethane Foam Production Polyamide Resin Production Polyphenylene Sulfide Production Polyacetal Production	Amino Resins Polycarbonates (linear thermoplastic polyesters) Epoxy Resins Polyester Resins (mixtures of unsaturated polyester resin and vinyl-type monomers) Alkyd Resins Polyethylene Terephthalate Nylon 6 Nylon 66 Polyurethane Foam Polyamide Resins Polyphenylene Sulfide Polyacetal Resins
Suspension Addition Polymerization			

\*Adapted from *Industrial Process Profiles For Environmental Use: Chapter 10, Plastics and Resins Industry*. Industrial Environmental Research Laboratory. Office of Research and Development. U. S. Environmental Protection Agency. Cincinnati, Ohio.

Table 3. Resin vs. Manufacturing Process

Resin \ Process	Mass	Suspension	Emulsion	Solution and Precipitation	Condensation
ABS/SAN			A		
Acetal	A	B			
Acrylic	A	B	B	A	
Polyethylene					
Hi-Density		A	A	A	
Low-Density	A				
Polystyrene	A	A	B	B	
Polypropylene				A	
Polyvinyl Acetate	B	B	A	B	
Polyvinyl Chloride	B	A	B	B	
Phenolics					A
Aminoplasts					A
Polycarbonates					A
Epoxy					A
Polyester					A
Polyamide					A
Polyurethane					A
<u>Elastomers</u>					
Butyl			A		
Ethylene-Propylene				A	
Neoprene			A		
Nitrile			A		
Polybutadiene			A	A	
Polyisoprene				A	
Styrene-Butadiene			A	B	

A - Process of primary industrial importance

B - Process of secondary industrial importance

## RESEARCH RECOMMENDATIONS

The following problem areas are identified as likely candidates for research and development by NIOSH. These problems were selected for consideration by NIOSH because of the following:

- Their resolution would result in a significant reduction in potential worker exposure.
- They are common to various segments and processes throughout the plastics and resins industry.
- They can be resolved based on existing state-of-the-art technology with minimal demands for new research.
- The actual research, development and implementation costs appear to be commensurate with expected results.

The selected problem areas fall into four general technical discipline areas involving systems analysis, mechanical engineering design, research and testing and ventilation control.

### SYSTEMS ANALYSIS

#### Safe Work Practices

An analysis of manufacturing plant problems from a systems analysis point of view often pinpoints problem areas that have simple non-technical solutions. One such area involves work practices.

Good work practices can be an important means of reducing worker exposures. The effectiveness of work practices in reducing worker exposure for similar operations at the various plant sites visited varied considerably. These variations could be qualitatively attributed to considerations such as educational level of workers, attitude of management, the physical appearance of the work environment, philosophy about housekeeping, and age level of workers.

Research is needed to quantitatively define the essential features that make work practices most effective. These findings could then be used as guidelines by management when planning work procedures with first line supervisors and workers.

#### Real Time Monitoring Instrument Systems

Most manufacturing plants that invested in the development and implementation of engineering controls have incorporated some form of instrument

systems for monitoring worker exposure. Two such systems are described in Appendices A.15 and A.16. The selection, implementation and operation of such systems require a substantial capital investment and high technical skill levels that may be out of reach for the smaller manufacturing plants.

Instrument systems with greater capability and substantially lower installed costs, and simpler operator interfacing requirements would be welcomed by both large and small industrial firms. Prior to the initiation of any research in this area, a comprehensive state-of-the-art study of monitoring instrument systems should be undertaken to quantitatively assess areas of greatest need. The technology in some of these areas is quite sophisticated and is undergoing a rapid change towards producing less expensive and easy-to-operate equipment that has incorporated diagnostic circuitry and software and adaptive algorithms for specific applications.

#### Computer Control of Processes

A higher degree of automation and computer control of the processes would reduce human errors that result in worker exposure to hazardous substances. The computer systems should also interface with the monitoring instrumentation and be programmed to identify work areas and procedures that have high incidences of worker exposure. This information could then be used by management to focus their efforts in upgrading the work stations, improving work procedures and providing additional training for the workers involved.

#### MECHANICAL ENGINEERING DESIGN

A number of problem areas that result in significant worker exposure could be resolved by better mechanical design of existing equipment (mechanical seals, blind flanges) or design of new equipment (pipeline cleaners).

#### Improving Double Mechanical Seals

A large PVC manufacturing facility may have up to 100 pieces of equipment (e.g., pumps, compressors) that require double mechanical seals in order for VCM concentration to be kept at acceptable levels. Experience has shown that seals exposed to process streams containing VCM will last from 2 months to more than 1 year depending on the application.

Improvements in the performance of double mechanical seals would significantly reduce the potential for worker exposure in plants already using some of the best engineering controls in complying with strict Federal regulations. A research and development program aimed at improving the performance of mechanical seals might begin by addressing such questions as:

- Why do given models of double mechanical seals, used in the same VCM applications, but in different vendors' equipment, fail at substantially different time intervals?
- Why do double mechanical seals manufactured by various vendors have different life times in given pieces of equipment?



## Isolation of Reactor Vessels with Blind Flanges

Blind flanges are installed in all lines entering a reactor vessel before workers enter the vessel for inspection or maintenance purposes. When the blind flanges are installed or removed manually, any hazardous material accumulated in the connecting lines is likely to be released into the immediate work area.

A reliable automated blind flanging system is needed to reduce the risk of worker exposure during maintenance on process equipment. The system should have the following features:

- Valves should be provided to safely vent any accumulated hazardous material.
- The flange assembly, drain valves and nearest process valve should be pneumatically or electrically actuated.
- All actuators on valves and blind flanges on the dead-ended line should be interlocked to assure the proper sequence of operation.

## Cleaning of Plugged Pipe Lines

A recurring problem in many plastics and resin manufacturing plants is plugging of pipelines with lumps of resin or reaction by-products that break away from surfaces inside the polymerization reactors. In many instances, it is virtually impossible to purge the hazardous vapors from the plugged pipe sections, prior to dismantling and cleaning.

A useful mechanism that needs to be developed for unplugging pipes is a pipeline router assembly that can be readily attached, as needed, to special fittings on the pipeline. To be of practical value to production personnel, the pipeline router assembly should have the following features:

- The design should be compact.
- The assembly should be easily connectable to the pipeline.
- A rotating probe must be able to enter the pipeline through a valving arrangement that provides open communication between the inside of the pipeline and the mechanism used for rotating the router once it enters the pipeline.
- The router should have flexible cutting blades that can cut through the obstruction and also scrape the pipe walls.
- A means should be provided for delivering a stream of water near the router in order to flush the smaller fragments produced when the router passes through the obstruction.
- A watertight seal should be located around the drive cable used to rotate and push the router through the pipeline.

- The special fitting attached permanently to the pipeline should be of a design that does not encourage accumulation of solids.

## RESEARCH AND TESTING

### Controlling Minor Additives in Polymerization Processes

Each polymerization process requires the addition of small amounts of additives such as catalysts, inhibitors, modifiers and antioxidants to the reacting mass to control or alter the reaction to a desired end. Several factors contribute to the extreme complexity of this potential health hazard:

- There are thousands of commonly used minor ingredients and most have not been the subject of toxicological evaluation.
- Many of the additives are purchased as trade name products, so there is difficulty determining the specific ingredients.
- Most manufacturing plants consider their additive systems proprietary.
- The fate of the additives during the polymerization reaction is either unknown or known only to the plant chemists.
- The effectiveness of the controls used during automatic and particularly during manual operations is difficult to quantitatively assess because the exposure times are very small and varied, and many times there are no available control limits for comparison.

These problems prevented a comprehensive evaluation of the many control techniques used during these operations in polymerization plants. The potentially high toxicity of some of the minor additives makes a detailed study highly desirable. The study should include several tasks:

- A comprehensive evaluation of the physical, chemical and toxicologic natures of the additives used in the industry. (This may involve recommendations for toxicologic research on common additives for which there are no available data.)
- A thorough evaluation of the effectiveness of engineering work practice control techniques for every method of adding polymerization ingredients.
- The development of a report that details each type of control technique, and qualitatively rates the control effectiveness (e.g., high, medium, or low). (For the more common toxic ingredients, an assessment of recommended control techniques should be made.)
- An evaluation of the fate of minor ingredients as the reaction proceeds to completion. (This is necessary to determine whether toxic intermediates or reaction products are produced, which could pose a health hazard to employees during reactor cleaning or downstream operations.)

## Corrosion Problems Following VCM Stripping

Some PVC manufacturing companies are observing that the techniques developed for stripping the VCM from process streams after the PVC polymerization reaction appear to aggravate the equipment corrosion problems. The high temperatures and extended residence time during degassing of the process stream apparently alter the chemistry of the process in a manner that causes the formation of undesirable compounds, resulting in not only increased corrosion, but also eventual process valve leaks.

A program is needed to identify the undesirable chemicals formed during VCM stripping and to establish the reaction mechanisms for their formation. A knowledge of the reaction mechanisms involved could lead to the development of methods for controlling the corrosion of process equipment.

## Considerations for New Plants and Processes

Much of the control technology described in the case studies is applicable to both new plants and processes and expansion and renovation of existing plant facilities. If reasonable and practical specifications are established by management for the process area environments, prior to the beginning of a plant design, the process design team could then produce the most cost effective overall plant design. A good example of this is described in Case Study No. 11, where the plant is being renovated to optimize production, while greatly improving the protection of the workers during normal operation and maintenance. (Note that it is recognized that this example is described simplistically, but it is actually being implemented based on production goals and economic constraints.)

## VENTILATION CONTROL

Of prime importance is the development and distribution of a reference document, describing those maintenance requirements necessary to keep a local ventilation system operating at design specifications. As noted in Appendix A.14, poor maintenance of ventilation systems in compounding operations is as much a problem as poor design. This document should explore the reasons for neglected maintenance and, using many industry examples, propose a maintenance protocol that can be enforced.

## SUMMARY AND CONCLUSIONS

This study is the first in a series of industry specific engineering control technology assessments based on a case study approach. The following conclusions are followed by a short summary of points to consider when extrapolating the control technology information.

1. The case study approach is an excellent method of assessing the state of industry-wide controls, particularly in the plastics and resins industry.
2. Polymerization processes are such that a control system for one process is frequently applicable to an entirely different process. The same is true for similar processes (based on reaction chemistry), which are used in the manufacture of dissimilar polymeric materials. Thus, much of the technology involved in a sophisticated control system, such as those depicted for exposure reduction to vinyl chloride, often can be applied to most of the plastics and resins industry. However, differences in physical properties (e.g., volatility, solubility) must be considered when attempting to apply the vinyl chloride control technology to processes utilizing monomers of low volatility, such as acrylonitrile.
3. The results of this study are useable as a reference resource by both government and industry personnel. The Users Guide and Subject Indices will allow rapid location of desired technical information, without the requirement for extensive subject matter review. Potential users of this assessment include industry management, health personnel and engineers, labor officials and industrial hygienists, federal compliance officers and control equipment manufacturers.
4. The studies of the PVC industry demonstrate that with sufficient time, capital resources and technical expertise, a significant reduction in worker exposure can be attained. The achievement of exposure levels below 1 ppm of vinyl chloride is possible through existing engineering control technology. With the recent concern for employee exposure to acrylonitrile, some of the vinyl chloride control strategies outlined in the document may be of immediate benefit to the ABS industry and others.
5. The extent of personal protective equipment usage is closely related to extremely strict requirements in federal health standards such as those for vinyl chloride and asbestos. Where these standards are applicable in the industry, there are generally well developed personal protection programs. However, where health standards are not yet promulgated, the programs are marginal, and use of protective clothing and respirators is generally based on personal preference.
6. Exposure to high noise levels is not a severe problem in the plastics and resins industry with the exception of compounding operations involving grinders, pelletizers or dicers. This is reflected in the relatively few instances of noise abatement techniques observed during the course of the study. Pumps and compressors can be a significant noise source, but are usually located in isolated areas and exposure times are limited.
7. The compounding industry yielded few examples of effective control technology. This is judged to be partly a result of poor maintenance

and the lack of application of existing control technology, and partly a lack of control technology.

An extrapolation of the control technology described in this report to other industrial applications must be done with care. In addition to industrial hygiene concerns, other factors such as those listed below must be considered:

- Physical and chemical properties of the hazardous material to be controlled
- Physical and chemical properties of the process stream that is the emission source
- Limitations of process parameters (e.g., temperature, pressure, reaction time)
- Is the control technology being implemented in an existing plant?
- Relative locations of other equipment and potential emission sources

Retrofitting of engineering controls into existing operations often presents serious obstacles to the industrial hygienist and the process engineer because of equipment location, plant configuration and space limitations. Great opportunities exist for process designers to provide a safer worker environment in new plants. However, the designer must be made aware of existing and proposed OSHA regulations and be familiar with control technology such as described in this report.

## USER GUIDE AND SUBJECT INDICES

This study was designed to provide pertinent engineering control information to a broad audience, including industrial plant health/safety officials and process engineers, OSHA compliance officers and health standards development personnel, engineering control equipment manufacturers, industrial hygiene consultants, and others.

It is clear that each of these intended users may be interested in different phases, or aspects, of this study, and generally will not have the specific need to review the entire document to locate the desired information. Therefore, a comprehensive set of indices follows that allows rapid location of particular information based on: 1) plastic or resin product, 2) industrial process, 3) toxic chemical or harmful physical agent, and 4) type of engineering control, work practice, or personal protective equipment. In addition to providing the location of information in this text, the indices offer a selective listing of pertinent references in the literature.

# INDEX I. Plastic or Resin Product

Product	Location in Document	Pertinent References
Acrylonitrile Butadiene Styrene (ABS) Resin	Case Study 6, page 100	---
Epoxy Resin	Case Study 11, page 144	Broughton 1965; Sargent et al. 1976, Kingsley 1958
Phenol Resin	Case Study 9, page 129 Case Study 10, page 134 Case Study 13, page 165 (compounded phenolic resin)	Schoenberg 1975
Polystyrene Resin	Case Study 7, page 114	DeGesero 1974
Polyvinyl Chloride Resin	Case Study 1, page 30 Case Study 2, page 45 Case Study 3, page 60 Case Study 4, page 71 Case Study 5, page 86	Hantell et al. 1975; Mack 1975; Wheeler et al. 1975; Goss et al. 1953; Rowe 1975; Cook et al. 1971; Plastics World 1976; Chemical Week 1976b; Chemical Week 1976d; Oil and Gas Journal 1976; Chemical Engineering 1975a
Styrene-Butadiene Rubber (SBR)	Case Study 8, page 120	Mallette 1943; McCormick 1971; Osman et al. 1972; Chemical Week 1976c; National Institute for Occupational Safety and Health 1976; Environmental Protection Agency 1975
Toluene Diisocyanate (TDI)	Case Study 12, page 160	Boyle et al. 1963
Polyester Resin	---	Bourne et al. 1963; Chemical Engineering 1974

\* No pertinent reference readily available.

## INDEX II. Manufacturing Process

Process	Location in Document
Bulk Polymerization Process	Case Study 1, page 30 Case Study 2, page 45 Case Study 7, page 114
Suspension Polymerization Process	Case Study 3, page 60 Case Study 5, page 86 Case Study 6, page 100
Dispersion Polymerization Process	Case Study 4, page 71 Case Study 5, page 86 Case Study 8, page 120
Condensation Polymerization Process	Case Study 9, page 129 Case Study 10, page 134 Case Study 11, page 144
Compounding Process	Case Study 13, page 165 Case Study 14, page 179



# INDEX III. Toxic Chemical or Harmful Physical Agent

Subject	Location in Document
Acrylonitrile	Case Study 6, page 100
Asbestos	Case Study 14, page 179
Benzene	Case Study 8, page 120
Bisphenol A	Case Study 11, page 144
Butadiene	Case Study 6, page 100 Case Study 8, page 120
Cadmium	Case Study 14, page 179
Chromium	Case Study 14, page 179
Diglycidyl Ether of Bisphenol A	Case Study 11, page 144
Epichlorohydrin	Case Study 11, page 144
Formaldehyde	Case Study 9, page 129 Case Study 10, page 134 Case Study 13, page 165
Hydrogen Chloride	Case Study 12, page 160
Lead	Case Study 14, page 179
Monochlorobenzene	Case Study 12, page 160

# INDEX III. Toxic Chemical or Harmful Physical Agent (continued)

Subject	Location in Document
Noise	Case Study 1, page 30 Case Study 4, page 71 Case Study 5, page 86 Case Study 6, page 100 Case Study 7, page 114 Case Study 14, page 179
Phenol	Case Study 9, page 129 Case Study 10, page 134 Case Study 13, page 165
Phosgene	Case Study 12, page 160
Polyvinyl Chloride Dust	Case Study 1, page 30 Case Study 2, page 45 Case Study 3, page 60 Case Study 4, page 71 Case Study 5, page 86
Sodium Hydroxide	Case Study 12, page 160
Styrene	Case Study 6, page 100 Case Study 7, page 114 Case Study 8, page 120
Talc	Case Study 8, page 120
Toluene Diisocyanate	Case Study 12, page 160
Vinyl Chloride	Case Study 1, page 30 Case Study 2, page 45 Case Study 3, page 60 Case Study 4, page 71 Case Study 5, page 86
Xylene	Case Study 10, page 134

## INDEX IV. Control Techniques

Control Techniques or Exposure Source	Case Studies or Pertinent References	
	Case Study or Reference	Summary
Storage Facilities Tank Farm Chemical Handling  Waste Storage	Case Study 2, page 45	• Convenient swivel jointed tank car unloading lines
	Case Study 11, page 144	• Solid catalyst vacuum loading facilities, • Specifications for tank car loading arms
	Case Study 12, page 160	• Storage and removal of solid waste residues
	Case Study 12, page 160	• Tank car filling
	Van Ingen 1974	• Collection of emissions from the top end of "slip gauge"
		• Recovery of collected monomer
	Oelfka 1974	• Use with sonic detector
	Wiley 1973	• Use with magnetic detector
		• Collection and recovery or disposal of vented or displaced vapors
	Wheeler et al. 1975	• Control of in-transit vinyl chloride
Relief Valves and Rupture Discs	Case Study 1, page 30	• Dual blow-out discs with interlocks
	Case Study 2, page 45	• Dual blow-out discs with pressure relief and interlocks
	Van Ingen 1974	• Reseating safety valves
	Anderson 1975	• Connection of relief valve discharge to flare
	Ludwig 1973	• Specifications for bubble-tight seating and reseating of valves
		• Hard valve seat design
		• Collection of discharge
		• Positioning of rupture disc
	Chemical Engineering 1975 b	• Simple leak-detecting device for rupture discs

## INDEX IV. Control Techniques (cont'd.)

Control Techniques or Exposure Source	Case Studies or Pertinent References	
	Case Study or Reference	Summary
Pumps, Compressors, Valves, Flanges and other locations	Case Study 1, page 30	• Seals for compressors, pumps and agitators
	Case Study 2, page 45	• Seals for compressors, pumps and agitators
	Case Study 4, page 71	• Removal of process stream from pipe sections or system requiring maintenance
	Case Study 5, page 86	• Seals for compressors, pumps and agitators
	Case Study 6, page 100	• Seals for pumps, agitators, valves and flanges
	Case Study 7, page 114	• Seals for pumps and valves
	Case Study 9, page 129	• Location of pumps
	Case Study 11, page 144	• Pump splash guards, fail safe pumping system
	Case Study 12, page 160	• Pressurized mechanical seals
	Rothman 1973	• Compress packing for pumps, gaskets
	Danielson 1973	• Valve leakage
	Browning 1969c	• Screwed, welded and flanged fittings estimating loss probabilities
	Templeton 1971	• Valve installation, operation and maintenance
	Russell 1974	• Flange gaskets
	Fitzpatrick 1974	• Belleville springs on flange closures
	Baturin 1972	• General leakage from pressurized systems
	Chemical Engineering 1975c	• New valves, flanges, gaskets used at Swedish vinyl chloride plant
	Iammartino 1975	• Flange tightening, welded couplings, gasket investigation, pump seals
	Arnstein 1965	• Pumping liquids effectively
	Hile 1974	• Closing vents on compressor seals prevents losses
	Templeton 1971	• Valve installation, operation and maintenance
	Rothman 1973	• Gaskets and packing types, compositions, temperature limitations, chemical resistance, cost comparisons
	Russell 1974	• Safety in flange joints
	Browning 1969a	• New techniques for analyzing industrial risks
	Browning 1969b	• Calculating loss exposures
	Browning 1969c	• Estimating loss probabilities

## INDEX IV. Control Techniques (cont'd.)

Control Techniques and Exposure Source	Case Studies or Pertinent References	
	Case Study or Reference	Summary
Leak Detection	Case Study 1, page 30	<ul style="list-style-type: none"> <li>• Multipoint process gas chromatograph, portable hydrocarbon detector</li> </ul>
	Case Study 2, page 45	<ul style="list-style-type: none"> <li>• Multipoint process gas chromatograph</li> </ul>
	Case Study 3, page 60	<ul style="list-style-type: none"> <li>• Multipoint process gas chromatograph</li> </ul>
	Case Study 4, page 71	<ul style="list-style-type: none"> <li>• Multipoint process gas chromatograph, portable hydrocarbon detector, continual leak search</li> </ul>
	Case Study 5, page 86	<ul style="list-style-type: none"> <li>• Multipoint process gas chromatograph, portable leak detector</li> </ul>
	Case Study 12, page 160	<ul style="list-style-type: none"> <li>• Area monitors, personal monitors</li> </ul>
	Case Study 15, page 184	<ul style="list-style-type: none"> <li>• Real time monitoring with a Rapid Scan Michelson Interferometer, computer data processing for TWA determinations</li> </ul>
	Case Study 16, page 197	<ul style="list-style-type: none"> <li>• Monitoring instrument system employing a gas chromatograph sensor</li> </ul>
	Kleeberg 1974	<ul style="list-style-type: none"> <li>• Multipoint gas chromatograph, analyzer and recorder</li> </ul>
	Hoy 1974	<ul style="list-style-type: none"> <li>• Portable detectors</li> </ul>
	Van Ingen 1974	<ul style="list-style-type: none"> <li>• Portable detectors</li> </ul>
	Mudd 1974	<ul style="list-style-type: none"> <li>• Hydrostatic testing of piping, flanges, manways, etc.</li> </ul>
	Wheeler 1975	<ul style="list-style-type: none"> <li>• Leak testing for tank farm operations</li> </ul>

# INDEX IV. Control Techniques (cont'd.)

Control Techniques and Exposure Source	Case Studies or Pertinent References	
	Case Study or Reference	Summary
Local and General Ventilation	Case Study 1, page 30	<ul style="list-style-type: none"> <li>• Location of permanent local exhaust hoods, strategy for energy conservation</li> </ul>
	Case Study 2, page 45	<ul style="list-style-type: none"> <li>• General ventilation of two story production area</li> <li>• Free handling exhaust ducts in multi-story building</li> </ul>
	Case Study 3, page 60	<ul style="list-style-type: none"> <li>• General exhaust ventilation system in multi-level building housing reactor</li> </ul>
	Case Study 4, page 71	<ul style="list-style-type: none"> <li>• Pump and compressor floor</li> <li>• Local exhaust ventilation for batch mix tanks, homogenizer pumps, orifices, reactors, blend tanks, filter enclosures, wet cak bins, recovery compressors</li> </ul>
	Case Study 5, page 86	<ul style="list-style-type: none"> <li>• General exhaust of production area</li> <li>• Local exhaust ventilation of reactors, pumps, seals, filters</li> </ul>
	Case Study 6, page 100	<ul style="list-style-type: none"> <li>• General exhaust ventilation of two-story production area</li> <li>• Local exhaust ventilation of sample collection hoods and floc pots</li> </ul>
	Case Study 7, page 114	<ul style="list-style-type: none"> <li>• General exhaust ventilation of control room, floc pots, filters and dryers</li> </ul>
	Case Study 9, page 129	<ul style="list-style-type: none"> <li>• Local exhaust ventilation of extruders and pelletizers</li> <li>• Steam ejectors on kettles</li> </ul>
	Case Study 10, page 134	<ul style="list-style-type: none"> <li>• Resin cooling belt</li> <li>• Venturi tank vent scrubbers for mixing tanks and reaction kettles.</li> </ul>
	Case Study 12, page 160	<ul style="list-style-type: none"> <li>• Local exhaust ventilation for resin cooling pans</li> </ul>
	Case Study 13, page 165	<ul style="list-style-type: none"> <li>• Ventilation of hose nozzles, waste residue storage</li> <li>• Local exhaust ventilation of exposure sources in resin compounding process.</li> </ul>

# INDEX IV. Control Techniques (continued)

Control Techniques and Exposure Source	Case Studies or Pertinent References	
	Case Study or Reference	Summary
Local and General Ventilation (continued)	Boyle 1963	<ul style="list-style-type: none"> <li>• Predicting ventilation requirements for coating materials</li> <li>• Dust control in manufacture of vinyl plastics</li> <li>• Selecting in-plant dust control systems</li> <li>• Ventilation for bagging operations</li> <li>• Dust control for asbestos</li> <li>• Aspirator system for dry blend operations</li> </ul>
	Goss 1953	
	Owen 1974	
	Hama 1948	
	Goldfield 1974	
	Mack 1975	
	Owen 1974	<ul style="list-style-type: none"> <li>• "Flip top" exhaust arrangement for dumping 50-pound bags of pigment</li> <li>• Hood designs for weighing and mixing highly toxic materials</li> </ul>
	Stern	<ul style="list-style-type: none"> <li>• Handling lead compounds in PVC compounding plant</li> <li>• Flexible metal hose systems for loading movable containers; method for charging open mixers</li> <li>• Exhausted booth for manual loading of hoppers, bag filling and barrel filling</li> </ul>
	Goss et al. 1953 1963	<ul style="list-style-type: none"> <li>• Bag filling booth</li> <li>• Hood enclosure, pouring slots for bag filling</li> <li>• Preventing dust while filling powders</li> </ul>
	Hama 1948	
Sample Collection	Constance 1970	
	Food Engineering 1971	
	Case Study 10, page 134	<ul style="list-style-type: none"> <li>• Sample collection in cups entering through a valve</li> </ul>
	Environmental Protection Agency 1976b DeGesero 1974	<ul style="list-style-type: none"> <li>• Sample flash-purge</li> <li>• Close loop sampler for polystyrene process</li> </ul>

# INDEX IV. Control Techniques (continued)

Control Techniques and Exposure Source	Case Studies or Pertinent References	
	Case Study or Reference	Summary
Strainers and Filters	Case Study 1, page 30 Case Study 2, page 45 Case Study 3, page 60 Case Study 5, page 86	<ul style="list-style-type: none"> <li>• Exhaust ventilation of low and high pressure filters</li> <li>• Filter integral to reactor</li> <li>• Water flushing of cuno filters</li> <li>• Replacement of in-line strainer with a comminuter</li> </ul>
	Environmental Protection Agency 1975 b	<ul style="list-style-type: none"> <li>• In-line delumpers</li> </ul>
Reaction Vessels Systems, (opening frequency, cleaning, addition of materials, stripping of residual monomers)	Case Study 1, page 30 Case Study 2, page 45 Case Study 3, page 60 Case Study 4, page 71 Case Study 5, page 86 Case Study 8, page 120 Case Study 9, page 129 Case Study 10, page 134	<ul style="list-style-type: none"> <li>• Stripping monomers from resin</li> <li>• Reactor degassing prior to operator entry</li> <li>• Stripping monomers from resins</li> <li>• Stripping process</li> <li>• Reactor cleaning and degassing</li> <li>• Reactor cleaning frequency, cleaning procedure</li> <li>• Kettle cleaning, addition of materials</li> <li>• Automatic vessel cleaning</li> </ul>
	Mudd 1974 Environmental Protection Agency 1975 b Mantell 1975	<ul style="list-style-type: none"> <li>• Organic solvent circulation</li> <li>• General evaluation</li> </ul>
Contaminated Process Water	Case Study 3, page 60 Case Study 4, page 71 Case Study 5, page 86 Case Study 10, page 134	<ul style="list-style-type: none"> <li>• Stripping vinyl chloride from PVC resins</li> <li>• Waste water vapor containment</li> <li>• Process liquids disposal</li> <li>• Process water disposal</li> <li>• Sewer trunk system</li> </ul>
	Environmental Protection Agency 1975 b	<ul style="list-style-type: none"> <li>• General evaluation</li> </ul>



# INDEX IV. Control Techniques (cont'd.)

Control Techniques and Exposure Source	Case Studies or Pertinent References	
	Case Study or Reference	Summary
Handling, Weighing, Dumping of Dry Materials	Case Study 1, page 30	• Air conveyance of resin
	Case Study 2, page 45	• Transporting of resins
	Case Study 4, page 71	• Transferring wet cake from filters, air lock system for adding ingredients
	Case Study 11, page 144	• Catalyst unloading and charge system
	Case Study 13, page 165	• Handling of solids in compounding process
	Case Study 14, page 179	• Storage and handling of toxic additives
	Burke 1973	• Weighing bulk materials in the process industries
	Kraus 1969	• Pneumatic conveyors
	Uncles 1969	• Containers and packaging
	Case Study 2, page 45	• Polymerizer degassing, autoclave degassing, warning light system, housekeeping, reaction area operating procedures
Work Practices	Case Study 4, page 71	• Awareness and concern by management and operating personnel
	Case Study 5, page 86	• Reactor cleaning practice
	Case Study 8, page 120	• Dewatering, drying and baling areas
	Case Study 9, page 129	• Kettle cleaning
	Case Study 10, page 134	• Vessel heating with Dowtherm
	Case Study 11, page 144	• Cleaning process equipment equipped with drains, steam source, sight glasses
	Case Study 12, page 160	• Procedures during maintenance, clean-up of spills
	Case Study 13, page 165	• Dry additives operation in compounding, drumming solids, mixer charge booths, housekeeping

## INDEX IV. Control Techniques (cont'd.)

Control Techniques and Exposure Source	Case Studies or Pertinent References	
	Case Study or Reference	Summary
Noise	Case Study 1, page 30	• Mixing of water and steam, resin transfer blowers
	Case Study 4, page 71	• Blower intakes and outlets for air conveyance, local exhaust systems
	Case Study 5, page 86	• Noise sources identified
	Case Study 6, page 100	• Floc line blowers, pumps
	Case Study 7, page 114	• Pelletizer, pelletizer enclosure
	Case Study 14, page 179	• Pelletizers, dicers
	Cattanach 1974	• Meeting noise objectives in the plastics industry
	Case Study 1, page 30	• Air line respirators coordinated with alarms, cleaning autoclaves, work uniforms
	Case Study 2, page 45	• Air line respirators, work clothing
	Case Study 3, page 60	• Air line respirators
Personal Protective Equipment	Case Study 5, page 86	• Air line respirator and air packs coordinated with alarms, work clothes
	Case Study 6, page 100	• Conditions requiring use of respirators
	Case Study 8, page 120	• Combination dust and organic vapor respirator
	Case Study 10, page 134	• Air packs, chemical cartridge respirators, rubber suits, shields, clothing
	Case Study 12, page 160	• Air line respirator usage requirements
	Case Study 13, page 165	• Gauze respirators, clothing, ear plugs

## APPENDIX A.1. PVC MASS POLYMERIZATION PROCESS - CASE STUDY NO. 1

### PROCESS SUMMARY

As depicted in Figure A.1-1, the major steps in this process are prepolymerization, polymerization, monomer recovery and resin handling.

Prepolymerization involves the production of polyvinyl chloride (PVC) nuclei from vinyl chloride monomer (VCM) in an agitated, vertical cylindrical tank. The procedure is to manually feed small quantities of additives into the tank through a spout, then pump in the VCM from the tank farm. A catalyst is used to initiate the reaction.

When the desired VCM conversion level in the prepolymerizer (usually <10%) is reached, the batch is gravity fed into a horizontal cylindrical autoclave, where the polymerization reaction goes to completion. Agitation is provided by a ribbon blender in the autoclave. The heat generated during the reaction is removed by a reflux condenser located vertically along the autoclave axis, and by the water-jacketed vessel surface.

At the completion of the reaction, unreacted VCM is vented to the condensers and compressors located in the monomer recovery area. Further monomer is recovered by stripping the resin of any residual, unreacted VCM.

Most of the resin is transferred to the product collector automatically by connecting the air conveyance system directly to the autoclave. The remaining resin is removed manually, usually without having to enter the vessel. From the product collector, the resin is dropped into a hopper, then passed through several screens to standardize the PVC particle size. Oversize particles are diverted to a grinder and returned to the screens. The product PVC is pneumatically conveyed to storage or transferred to the compounding or bagging areas.

### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

#### Vinyl Chloride

TWA 1 ppm, ceiling limit 5 ppm for any 15-minute period

#### Polyvinyl Chloride Dust

TWA 15 mg/m<sup>3</sup> total dust

#### Noise

TWA 90 dBA

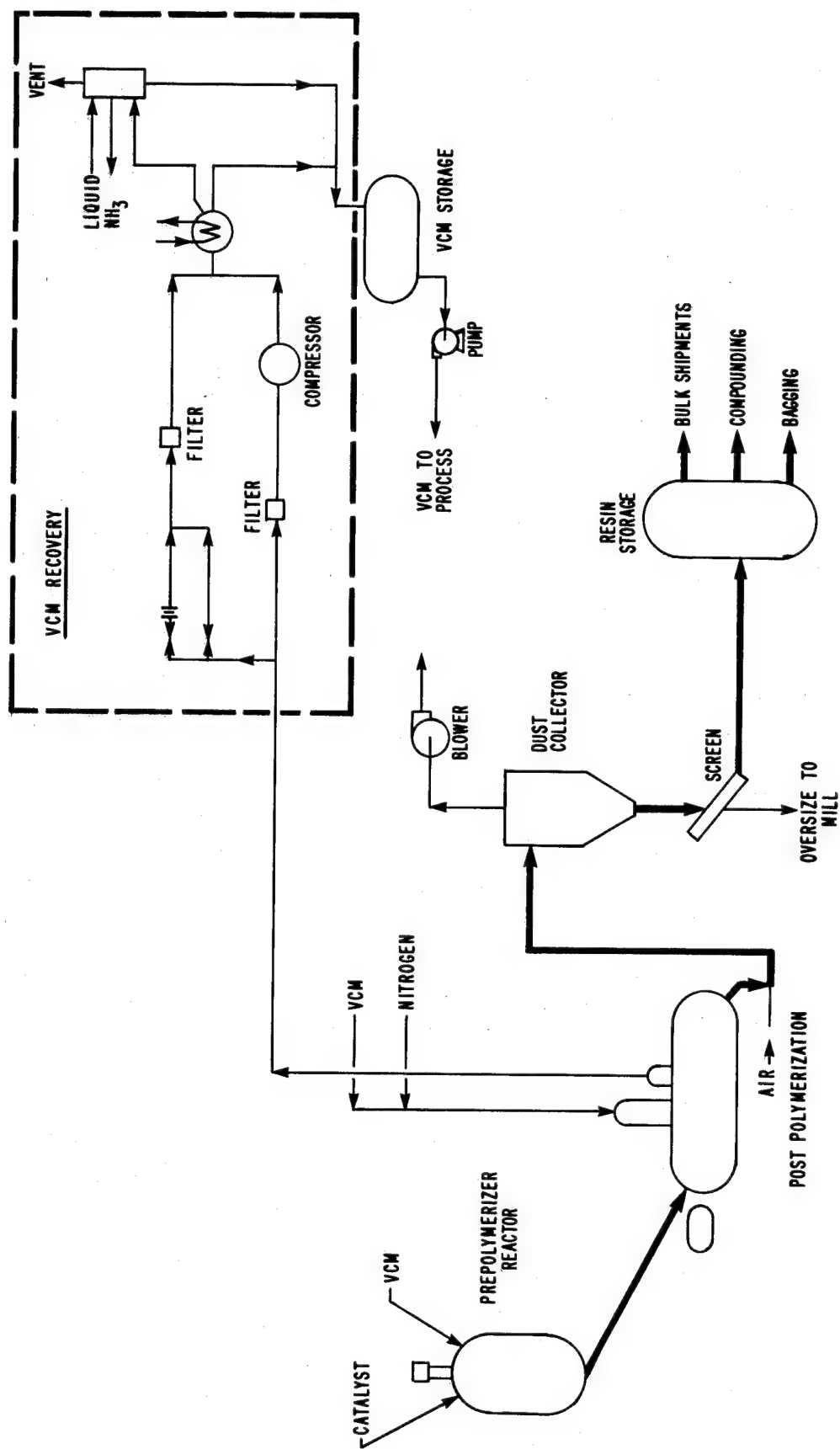


Figure A.1-1. Polyvinyl Chloride Plant Bulk Process Flow Sheet

## CONTROL OF VINYL CHLORIDE MONOMER

The VCM control system may be described under several headings:

- Process design, modification and maintenance
- Leak detection and prevention
- Local exhaust ventilation
- General ventilation
- Ongoing improvements

### Process Design, Modification and Maintenance

#### Inherent Operating Characteristics --

The inherent operating characteristics of the bulk polymerization process permit a relatively high degree of employee exposure control. The process is totally enclosed until the polymerization autoclaves are opened for resin transfer. At this point, residual VCM levels are exceedingly low because of the effectiveness of the stripping operation.

The most important characteristic of the bulk process is that the VCM does not have to be suspended or emulsified in an aqueous or solvent medium. This reduces the potential for employee exposure by:

- obviating the need for postpolymerization separation and drying operations;
- eliminating the exposure associated with solvent recovery or monomer-contaminated waste water disposal and treatment; and,
- allowing the use of low-temperature recovery condensers, which lessens the potential for leaks and decreases VCM concentration in the off-gas.

#### Computer Control of Process--

The process cycle is almost totally computer-controlled, thus reducing the possibility of significant VCM escape due to operator error or failure. When operator errors do occur during certain manual operations, the reasons are analyzed to determine if additional preventive measures can be integrated into the computer control system to eliminate recurrences.

In addition, computer control reduces both the number of on-site operators needed to run the process and their time spent in potential exposure areas. The on-site operators spend a large portion of their time in safe exposure areas, such as screening and grinding sites, and non-exposure areas, such as the positive pressure control room.

#### Bulk Process Reaction System--

The bulk process reaction system shown in Figure A.1-2 was designed to totally enclose the reaction and stripping steps and to reduce maintenance requirements on both the reactor and the VCM recovery equipment. The main features that

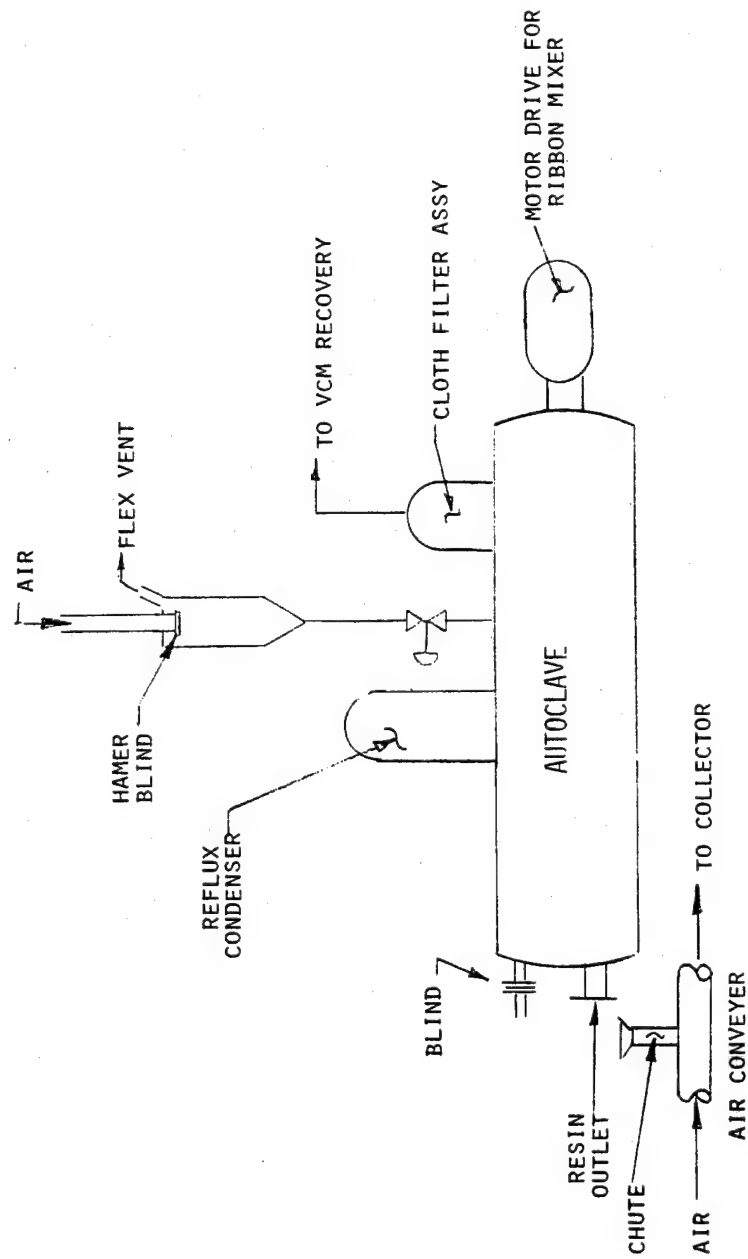


Figure A.1-2. Bulk Process Reactor

result in reduced worker exposure are the following:

Stripping process-- VCM stripping is undertaken in the autoclave following the polymerization cycle and is very important to the overall VCM control program. The general steps are as follows (refer to Figure A.1-2):

- At the completion of the polymerization cycle, multi-stage recovery compressors draw two successive vacuums on the autoclave.
- During each evacuation, the autoclave is heated to facilitate VCM removal from the resin.
- Nitrogen is used to break the vacuum after the first evacuation to prevent the formation of explosive VCM/air mixtures.
- Air is used to break the vacuum after the final evacuation.
- The autoclave is opened for resin transfer after the air pressures inside and outside the autoclave are equalized.

Heat removal-- In addition to the jacketed autoclave surface, a reflux vapor condenser is used to remove the heat generated during the polymerization reaction. Condensation of the VCM vapors on the condensers does not result in fouling of exchanger surfaces as would be the case if the exchanger were in direct contact with the liquid reacting mass. The need to enter the reactor vessel for maintenance purposes is therefore substantially reduced.

VCM vapor filtering-- The VCM vapor removed after the completion of the polymerization step must be free of particulates to avoid damage to compressors and peripheral equipment in the VCM recovery area. The filter assembly is housed (refer to Figure A.1-2) in a dome or manhead above the autoclave. The filter assembly consists of filter medium mounted on a 24-inch diameter coarse screen basket. Potential exposure due to opening and cleaning the filter is reduced by scheduling the cleaning after the autoclave stripping operation. An air conveyance system for the finished resin permits emptying of the reactor under negative pressure conditions. Therefore, the flow of air induced into the autoclave through the resin transfer manway prevents any residual monomer from escaping into the workplace.

#### VCM Recovery Operations--

The VCM recovery operation was designed to minimize the use of compressors and to reduce the load on the compressors. The recovery area is depicted in Figure A.1-1. The recovery cycle begins with the VCM at pressures substantially above the VCM condensation pressure. The VCM is passed directly to the condensers, until the system pressure drops to the VCM condensation pressure (40 psi). At this point, the valves on the lines bypassing the compressor are closed, the valve on the line to the compressor is opened and the remaining VCM is compressed to pressures above the condensation pressure and then condensed in the chilled condenser and returned to storage.

#### Dual Blow-Out Disc Interlocks--

Dual rupture discs (one under pressure and one spare) are employed on the prepolymerizers and autoclaves to minimize VCM loss to the atmosphere in the

event of a rupture disc blowout. The handles of the valves preceding these two rupture discs are interlocked so as to effect the automatic engagement of the spare rupture disc when the valve ahead of the ruptured disc is closed manually. This mechanical design feature prevents human errors that could result in significant VCM emissions during an emergency.

#### Prepolymerization Entry Procedure--

In order to minimize potential exposure when employees must enter the prepolymerizer, a vacuum of approximately 26 inches is pulled on the vessel, after which the vessel is pressurized to atmospheric pressure with nitrogen. Nitrogen is needed to avoid potentially explosive gas mixtures. This sequence is repeated twice. The second vacuum break is with air. To increase the effectiveness of this pre-entry procedure, there are plans to provide additional heating capacity to this vessel to assist VCM removal.

#### Vent Stack Location--

The vent stack outlet is located approximately 80 feet above the top of the process building. This stack height is designed to prevent vented VCM from re-entering this or any other process building by putting the outlet above the turbulence and eddies induced by the building. The vent stack is used to intermittently dispose of small quantities of VCM during normal operations and for venting VCM leaks until proper maintenance operations can be performed.

### LEAK DETECTION AND PREVENTION

#### Description of System

The process characteristics and modification described above preclude the extensive escape of VCM into the workplace. The major remaining exposure source is leaks from valves, flanges, compression pumps and agitator seals.

Rapid leak detection is an integral part of the VCM exposure reduction program. The detection system consists of two parts, each essential to the program's effectiveness:

- (a) Process Gas Chromatograph Monitoring System: Air samples are collected in sequence from a number of strategically located monitoring points (optimum locations determined by extensive area sampling). Each of the monitoring points is sampled every six minutes, and a continuous strip-chart recorder plots the VCM results calibrated in parts per million. Any individual reading from 1 ppm to 5 ppm activates a warning light in the control panel and in the process areas; a reading greater than 5 ppm activates flashing red lights. The light system simultaneously dictates respiratory protection requirements and initiates the leak detection procedure. A computer alarm is activated upon detection of any VCM concentration in excess of 900 ppm. If this occurs, an audio-alarm is sounded and buildings are evacuated.
- (b) Portable Hydrocarbon Detector: When any warning light is activated, a designated employee goes to the strip-chart recorder and determines which monitoring point recorded a VCM level in excess of 1 ppm. He then takes a portable hydrocarbon detector and uses it to locate the leak. If the leak has not stopped, or cannot be promptly repaired,



one (or more) of the available flexible exhaust hoses is opened and positioned to capture and exhaust the escaping VCM until maintenance personnel can correct the problem.

The conditions surrounding each leak are recorded and maintained. A periodic evaluation of these records serves to pinpoint recurring problem areas.

#### Important Equipment Features

The following equipment features reduce leak occurrence and result in a reduced potential for worker exposure:

- (a) Valves: Various types of valves have been evaluated for specific applications. In some instances, superior valves were found that reduced leaks and maintenance requirements. In general, most ball valves were phased out and replaced with butterfly valves.
- (b) Prepolymerizer: The agitator shafts have Pfaudler oil seals (refer to Table A.1-1) under nitrogen pressure greater than the maximum vessel pressure. It was reported that no replacements have been required for these seals in over 2 years and leaks are infrequent.

---

Table A.1-1. Seals for Compressors, Pumps and Agitators

---

Application and Vendor	Seal Manufacturer	Seal Model Number
Recovery of VCM Pennsylvania Compressor	Pennsylvania Compressor	Vendor will supply details.
Pump for VCM Duriron Model Mark II	Crane	Type 9T QPICI (316)
Agitator on Prepolymerizer	Crane	Type B
Autoclave-Ribbon	Pechiney- Saint Gobain	Vendor will supply details.

---

- (c) Autoclave: The ribbon-mixer drive shaft seal (refer to Table A.1-1) is packed with grease under a pressure of approximately 200 psi, which is greater than the maximum working pressure in the vessel. Preventive maintenance is required twice a week to make adjustments, which generally consist of manually adjusting the piston in the grease cartridge to maintain the required grease pressure. The packing usually lasts 1 year.

- (d) Compressor Seals: The recovery compressor seals (refer to Table A.1-1) are pressurized with nitrogen at a pressure greater than the VCM pressure. Any leaks in a seal result in nitrogen's passing into the monomer-recovery plumbing and a build-up of noncondensable gases ( $N_2$ , etc.) in the recovery system. The computer system will react to this situation by alerting the operators to check the compressor seal. However, compressor seal failure has been very rare.
- (e) Pumps: Pumps used for transporting VCM or process streams containing VCM are located outdoors. Teflon packing material is used in pump seals (refer to Table A.1-1) because of its resistance to VCM. Whenever possible, process streams are transported by gravity flow, facilitated by proper elevation of process vessels. This is an excellent example of alleviating a potential source of exposure by totally eliminating the need for leak-prone equipment.

#### LOCAL EXHAUST VENTILATION

The usual purpose of local exhaust ventilation systems in industry is to remove emissions of toxic contaminants from permanent process sources that cannot be controlled by process enclosure or other methods. As this process is fully enclosed and without permanent emission sources, a novel local exhaust strategy is necessary -- one flexible enough to deal effectively with multiple, periodic leaks occurring in a variable and unpredictable manner.

The system that has been evolved for this process is both effective and efficient from an energy-conservation standpoint. A total of 34 process points were selected for installation of permanent exhaust hoods or flexible-hose entry sleeves, on the basis of potential for leakage. Because many of the process points are identical and repeated for each operating line, the total number of distinct types of exhaust takeoffs is reduced to 11, as follows:

- (1) Autoclave filter manheads ( $.189 \text{ m}^3/\text{s}$  [400 cfm\*])
- (2) Vacuum brake valves ( $.104 \text{ m}^3/\text{s}$  [220 cfm] )
- (3) Autoclave drive end shaft seal ( $.189 \text{ m}^3/\text{s}$  [400 cfm] )
- (4) Recovery manifold bleed valve ( $.094 \text{ m}^3/\text{s}$  [200 cfm] )
- (5) Low-pressure VCM filters in the recovery area ( $.212 \text{ m}^3/\text{s}$  [450 cfm] )
- (6) High-pressure VCM filters in the recovery area ( $.212 \text{ m}^3/\text{s}$  [450 cfm] )
- (7) Prepolymerizer Yarway valves ( $.179 \text{ m}^3/\text{s}$  [380 cfm] )
- (8) Additives entry funnel ( $.142 \text{ m}^3/\text{s}$  [300 cfm] )
- (9) Autoclave shaft seal hood ( $.189 \text{ m}^3/\text{s}$  [400 cfm] )
- (10) All blind flanges ( $.156 - .189 \text{ m}^3/\text{s}$  [330 - 400 cfm] )
- (11) Recovery compressor ( $.283 \text{ m}^3/\text{s}$  [600 cfm] )

The first seven of these exhaust points consist only of a duct connection sleeve into an enclosure surrounding the individual piece of equipment.

---

\*These are design air flow rates used in calculations for estimating the required blower capacity, i.e., on the basis of these flow rates and the number of branches open at a given time the total cfm capacity was calculated. Actual flow rates are equal to or greater than design values.

The additives entry funnel exhaust (No. 8) consists simply of a flexible exhaust duct dropped into the funnel. The final three points consist of permanently affixed hoods that were custom designed to fit the geometry of the specific flange, autoclave and compressor. Each of the hoods and enclosures can be exhausted by connecting it with individually accessible flexible exhaust ducts (3' - 25' long) extending from a common main duct. An important secondary function of this system is the containment of leaks at process points other than those already listed. If there are no leaks in an area served by a given flexible duct, it is "deadheaded" or blocked off with metal plugs or branch dampers.

The distinctive feature of the system is that it is used solely as an adjunct to the leak detection and prevention program, i.e., the exhaust is provided to a given hood or enclosure sleeve on a "need" basis, when a leak is detected at that point.

The logic behind the system is simple and compelling. If the individual hoods or enclosures were exhausted constantly, leaks would be masked and could not be isolated and corrected, and the leak detection and prevention program would be circumvented. This would be unacceptable because the overall VCM containment strategy hinges on engineering modifications that will prevent leaks rather than exhaust them. An additional objection is the large expense of installing a system to clean exhausted air to meet the EPA requirements of no more than 10 ppm VCM in vented air. Such a system would be necessary if leaks were allowed to continue and control depended solely on local exhaust ventilation.

#### GENERAL VENTILATION

The general ventilation system depicted in Figure A.1-3 is not intended to be a primary means of control. Under normal conditions, the system provides approximately 19 air changes per hour during winter and 37 air changes per hour during summer and/or emergency conditions. The emergency ventilation system is operated manually when the gas monitoring system detects 900 ppm or more of VCM.

The system is designed to induce a relatively consistent airflow pattern from the south to the north end of the building. The exhaust fans are located on two levels to correspond to the two process areas, separated by an open grate floor. This assists in minimizing the amount of air flowing through the grating such that a leak in one process area will not cause high VCM levels in the other.

A solid floor was installed over the open grating between the penthouse and the main process building. This floor has eliminated VCM excursions into the penthouse by effectively segregating it from the process area where leaks may occur.

The benefits from the system are twofold. Of primary importance is the high air change rate which provides dilution to reduce VCM concentrations from process leaks. Also due to the location of the exhaust fans, leaks in one area do not usually exert a large contaminating influence on other areas due to the overall direction of the flow.

Fan	Air Flow m <sup>3</sup> /s		
	Winter	Summer	Emergency
RV29	0	3.30	3.30
RV30	0	3.30	3.30
RV32	0	1.75	1.75
EF42	0	0.654	0.654
EF46	1.75	1.75	1.75
EF39	3.30	6.61	6.61
EF40	3.30	6.61	6.61
EF41	0	6.61	6.61
EF45	0	6.61	6.61
EF54	6.61	6.61	6.61
EF55	6.61	6.61	6.61
Louvers	closed	open	open
Air change /hour	19	37	37

EF = exhaust fan

RV = roof ventilation

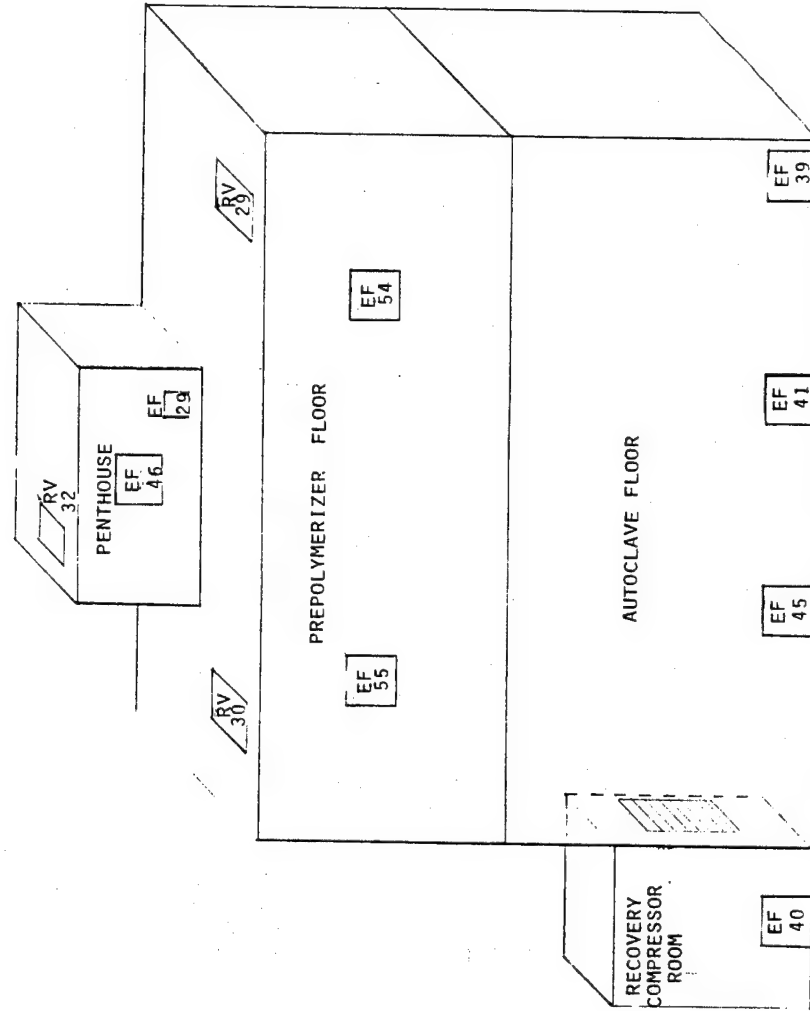


Figure A.1-3. General Ventilation

The VCM recovery room at the east end of the building originally was not partitioned off from the main building. It was determined that VCM leaks in this area were creating exposure conditions in other areas of the main building. Because this area is infrequently entered by personnel, the connecting space was almost totally partitioned with a block wall, causing a measured inward airflow of about 150 fpm through open sections in the partition. Since this modification, no further excursion levels have been induced by leaks from the recovery condenser or compressor.

#### ONGOING IMPROVEMENTS

The large majority of planned techniques are directed towards reducing environmental emissions in compliance with the newly promulgated EPA regulations for vinyl chloride. However, as is often the case, these improvements will also have a beneficial effect on worker exposure rates. Two major improvements have been planned:

- The installation of a treatment system for reducing VCM concentrations in air exhausted to the atmosphere from the recovery system to 10 ppm. Either a carbon adsorption or a solvent absorption treatment system will be installed.
- Better preparation techniques prior to opening reaction vessels. This is necessary to meet EPA's requirement of no more than .02 gram VCM (in vapor space of reactor) per kilogram of resin product. Improvements may include an increase in the number of successive vacuums pulled on the vessel prior to opening.

#### VCM MONITORING -- CONTROL SYSTEM EFFECTIVENESS

A full-scale VCM monitoring program was initiated in early 1974 and extensive data have since been developed. Area sampling data are provided by the process gas chromatograph monitoring system. From 1974 to early 1976, all data points were recorded and summarized as weekly averages. To illustrate the effect of implemented control measures, monthly area sample averages are plotted in Figure A.1-4. The reduction is apparent, particularly from 1974 to the first quarter of 1975 when most engineering controls were installed.

Since March of 1976, area sampling data have been summarized in terms of percent readings under 1 ppm, as follows:

<u>Month 1976</u>	<u>% Readings &lt;1 ppm VCM</u>
April	90
May	92
June	94
July	91
August	91
September	95
October	92

As shown, 90% or more of all VCM measurements are consistently below 1 ppm.

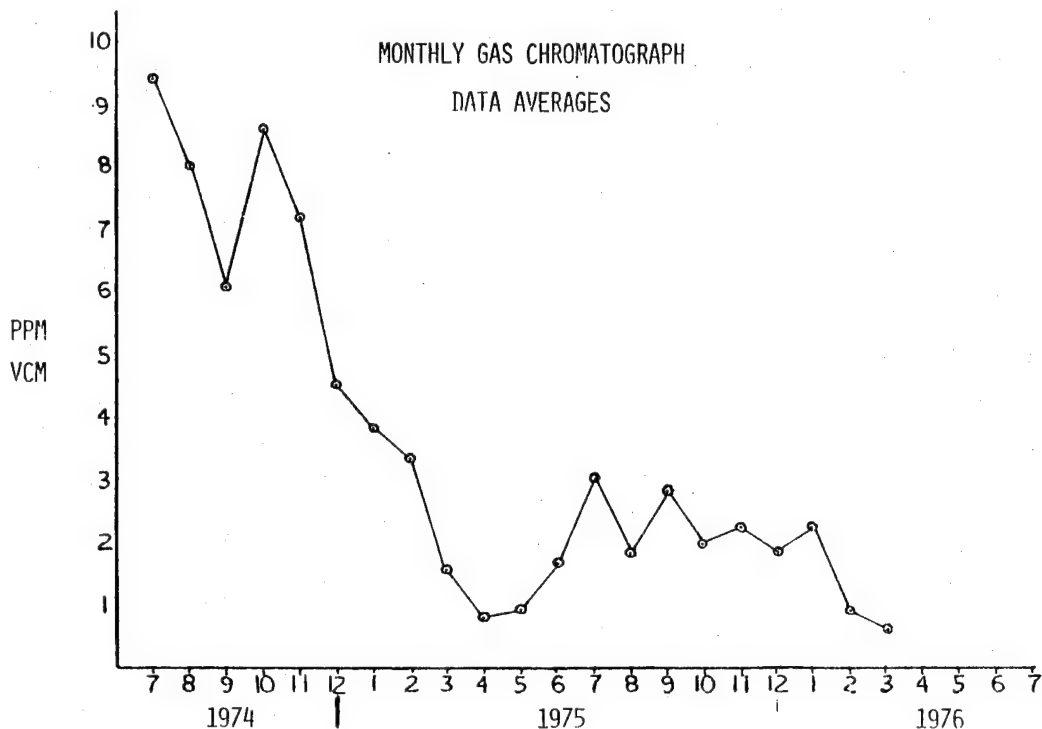


Figure A.1-4. Monthly Gas Chromatograph Data Averages

Each employee is also monitored every month with charcoal tube sampling devices. These samples are worn by the employee over a full shift and thus reflect actual 8-hour time-weighted average exposure.

The following summary lists averaged 8-hour time-weighted exposures of workers during 1974, 1975 and 1976.

Average Distribution of VCM Results

<u>Period</u>	<u>VCM parts per million</u>				
	<u>&lt;1</u>	<u>1-3</u>	<u>3-5</u>	<u>5-10</u>	<u>&gt;10</u>
1974	2%	34%	18%	22%	24%
1975	43%	37%	8%	9%	3%
1976	73%	17%	3%	5%	2%

The reduction of employee exposure level is apparent, particularly from 1974 to 1975. It was during this period that many of the engineering controls were installed.

It is unfortunate that there are no available data which reflect the relative effectiveness of each control technique that has been incorporated into the process system. However, it is clear that no one control is independently sufficient to meet the 1 ppm VCM standard. The combination of many techniques is necessary to achieve the degree of control seen to date.

The program to reduce VCM exposure is not yet complete. Efforts are continuing

to make better use of the currently installed controls and, where needs are pinpointed by the leak detection, additional controls are being implemented.

#### PERSONAL PROTECTION EQUIPMENT FOR VCM

The requirements for respiratory protection from VCM exposure have been integrated into the monitoring alarm-light system. Employees are required to use the full-face supplied air line system when the amber light (reading greater than 1 ppm) is activated. However, the employees may use a short air line and move from one air line connection to another. Respiratory protection is also required when workers are performing tasks that are known to cause exposures (i.e., changing flanges on VCM lines or entering process vessels). When the flashing red light (greater than 5 ppm) appears, the full-face supplied air line system again must be used, but a long air line is required and mobility is decreased. If the monitoring system picks up a reading of greater than 900 ppm, an alarm is sounded and the building is evacuated. In this situation, a self-contained air pack is required for re-entry.

When employees enter an autoclave for cleaning, a Tyvek<sup>®</sup> suit, a hood and work gloves are required.

Work uniforms are provided daily and showers are recommended, but not required.

#### CONTROL OF OTHER POTENTIAL HAZARDS

##### PVC Dust

PVC resin may become airborne from leaks in the screening and grinding system. This is considered nuisance dust with a permissible time-weighted average exposure limit of 15 mg/m<sup>3</sup>. Dust control is effected by maintaining the enclosed integrity of the screens and grinder, by ensuring good mechanical fits, and by keeping all enclosures under a slight negative pressure. The latter is accomplished by providing small ducts from the pneumatic transfer system to the hoppers, screens and grinders. Horizontal surfaces are periodically cleaned of settled resin with industrial-grade vacuums. Operators rarely have to enter these areas, so isolation is considered a very effective control.

##### Noise

Noise readings in the polymerization building average from 90 dBA to 92 dBA. The major sources of this noise are the agitator motors for the prepolymerizers and autoclaves, and one steam mixer that has not been modified as in Figure A.1-5. Due to the fact that the operators' average exposure time in the area is less than 4 hours per day, hearing protection is not legally required. However, plant safety and health personnel feel that no extended (>1 hour) exposure is tolerable and hence require hearing protection for employees who will be in the reaction area in excess of 1 hour at a stretch. Only two noise-abatement control modifications were noted. The mixing of cooling water with high-pressure steam in a pipe was causing very high noise levels and induced substantial line vibration. This situation was corrected by relocating the steam mixing jets on the inlet side of the pump (refer to Figure A.1-5). Before-and-after sound-pressure levels were not available for comparison, but discussions with various operators indicated that this

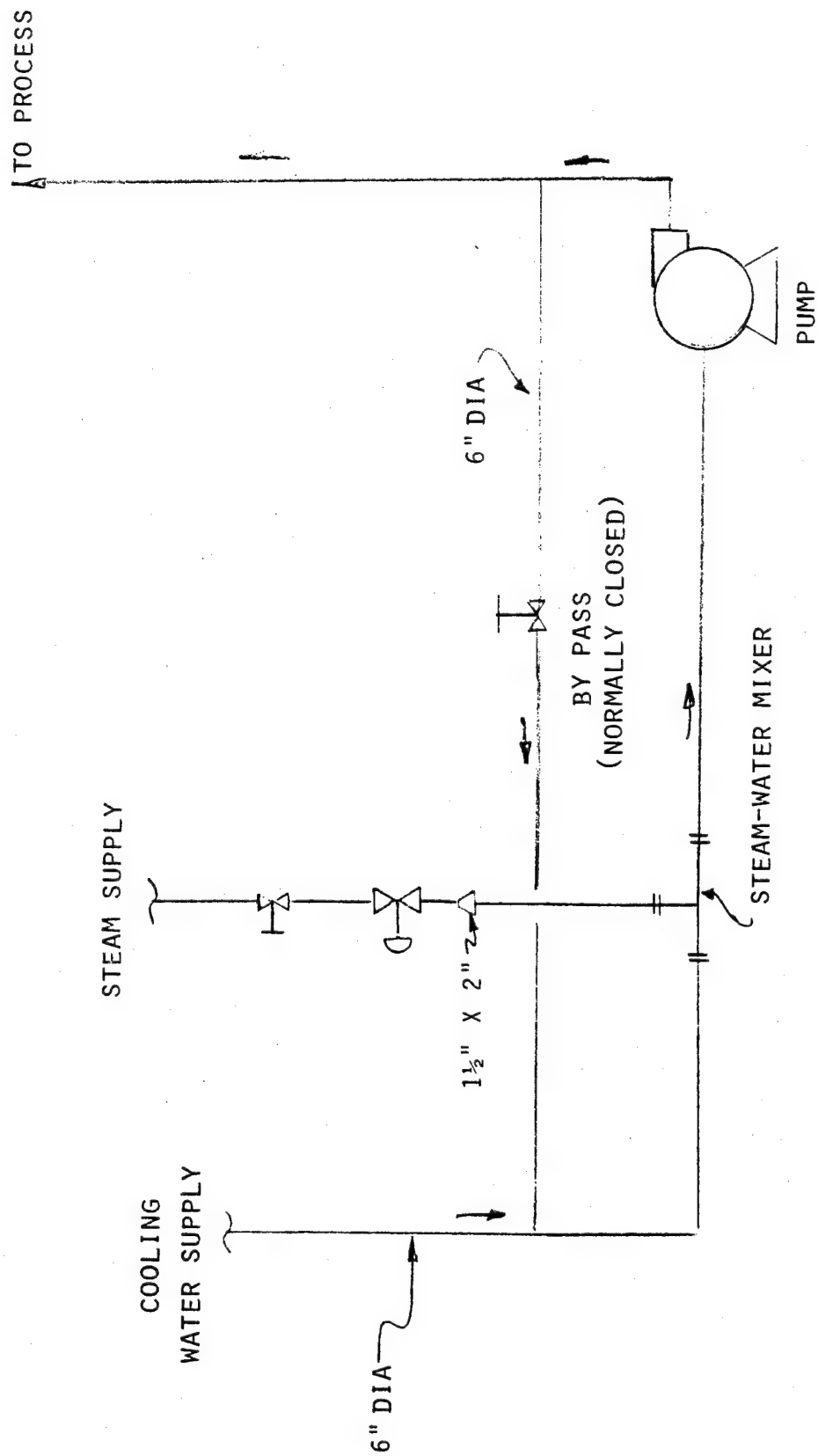


Figure A.1-5. Steam-Water Mixer



modification was very successful.

The resin transfer blowers (located outside) were exceptionally noisy. These blowers were totally enclosed in a block house. Noise levels in these areas were reduced to well below 90 dBA.

## APPENDIX A.2. PVC MASS POLYMERIZATION PROCESS - CASE STUDY NO. 2

### PROCESS SUMMARY

A simplified flow diagram of this bulk polymerization process is depicted in Figure A.2-1.

Prepolymerization involves the production of polyvinyl chloride (PVC) nuclei from vinyl chloride monomer (VCM) in an agitated vertical cylindrical vessel. After vacuum testing the prepolymerizer, the catalyst is dropped into the vessel and rinsed with mineral spirits. The VCM is then pumped in, and the reaction is initiated by heating the vessel jacket. At the proper point, the jacket is switched to the cooling mode and the condenser is turned on to assist in removing the heat of reaction.

When the VCM conversion level reaches 8-12%, the slurry is gravity fed into an agitated, horizontal cylindrical autoclave which serves as a postpolymerizer. The autoclave is also vacuum tested prior to receiving the prepolymerizer charge. The heat generated during the reaction is removed by a reflux condenser, a jacketed vessel surface and the water cooled agitator blades. The reaction goes to completion in 4 to 5 hours, and the reactor is repeatedly depressurized to remove and recover residual VCM.

The PVC resin is transferred to the product collector by opening a discharge port and connecting it to a pneumatic conveyance system. The last bit of resin is swept out by the airflow induced by opening a butterfly valve at the opposite end of the autoclave.

From the product collector, the resin is dropped into a series of screens and crushers to standardize PVC particle size and classify different grades of resin. Finally, the PVC is pneumatically conveyed to storage for future bulk shipment or transfer to the compounding plant.

### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

#### Vinyl Chloride

8 hour TWA 1 ppm, ceiling limit 5 ppm for any 15-minute period

#### Polyvinyl Chloride Dust

8 hour TWA 15 mg/m<sup>3</sup> total dust

#### Noise

8 hour TWA 90 dBA



## CONTROL TECHNIQUES

### Process Design, Modification and Maintenance

The advantages relative to hazard control of the bulk polymerization process are presented in detail in Appendix A-1. In summary, the inherent operating characteristics of the bulk process effect a reduction of employee exposure potential by:

- obviating the need for postpolymerization separation and drying operations;
- eliminating the exposure associated with solvent recovery or monomer-contaminated waste water disposal and treatment; and,
- allowing the use of low-temperature recovery condensers which lessens the potential for leaks and decreases VCM concentration in the off-gas.

### Process Control--

Mechanical stepping switches are used to control valve operation, pressure switches, weight set points, analog controller set points and other sequential operations. The mechanical sequencer will not proceed until clearance is received from process condition sensors or from a switch triggered by the operator. The operators are thus required to interact with the control system in certain critical process steps. This assists in reducing the potential for upset conditions which could lead to large releases of VCM by the avoidance of manual operation of process equipment. It also reduces the number of operators necessary to run the process.

### Enclosed Control Room--

All process controls are located in an enclosed control room under positive pressure from an independent air handling system. As an average, employee time distribution is as follows:

<u>Job Title</u>	<u>Percent Time in Control Room</u>
Superintendent	75%
Foreman	75%
Operators	95%
Asst. Operators	75%
Autoclave Cleaners	10%
Utility Employees	15%

Since the VCM concentration is essentially zero in the control room, most employees are isolated from the exposure area for a large segment of the shift. Obviously, this is a most effective control technique.

### Prepolymerizer Degassing Operation--

The degassing procedure for this vessel is dependent on whether operator entry is planned following the cycle. If entry is not required, a single vacuum to 2.6 psia is pulled by the two-stage recovery compressor and the residual VCM goes to the recovery system. The catalyst is introduced through an airlock and a minimal amount of air is introduced. Vacuum is not broken and the vessel is ready for another charge.

If operator entry is required (approximately once per day), a multiple degassing sequence is required. First, the recovery compressor draws a vacuum to 2.6 psi, followed by a nitrogen break. Next, a vacuum pump draws sequential vacuums to 2.1 psi, first breaking the vacuum with nitrogen, then with air. The manhole is opened and a flexible duct exhaust is immediately inserted. Prior to entry, the vessel air is checked for VCM concentration. Obviously, the multiple degassing sequence reduces VCM escape when the manway is opened for entry. Although employees who enter the vessel are required to wear respiratory protection, minimizing VCM concentrations reduces the exposure potential for these employees also.

#### Autoclave Degassing Operation--

A three-stage degassing procedure is used to remove residual VCM from the vessel vapor space and the PVC resin. First, the vent line valves are opened, allowing the autoclave pressure to force VCM vapor to the recovery condenser. This process continues until the pressure has been reduced to 70 psi, at which time the recovery compressor is started. The compressor pulls vacuum to 2.6 psia and the steam stripping operation is begun. After a time, the vacuum pump is activated and the autoclave pressure is reduced to 2.1 psia (depending on the resin, the steam may be cut off prior to the vacuum pump activation). Nitrogen is used to break the vacuum to slightly below atmospheric pressure and the resin is then ready for transfer. Prior to operator entry, the nitrogen is removed by airflow induced by the resin transfer operation.

This process removes virtually all VCM from the autoclave vapor space and reduces residual VCM in the resin to below 400 ppm. The VCM in the resin diffuses very slowly over a long period of time so that VCM concentrations around all downstream operations are greatly reduced and the potential for further exposure is essentially eliminated. As with the prepolymerizer degassing process, potential exposure to VCM when employees open and enter the vessel is reduced substantially.

#### VCM Vapor Filter--

The VCM vapor removed during the degassing cycle must be free of particulates to protect the compressors and other equipment in the recovery system. The filter assembly is mounted in a dome or manhead above the autoclave. Hence, when the autoclave is degassed, the filter assembly is similarly stripped of residual VCM. Hence, filter opening and cleaning operations are scheduled following degassing and potential employee exposure is reduced.

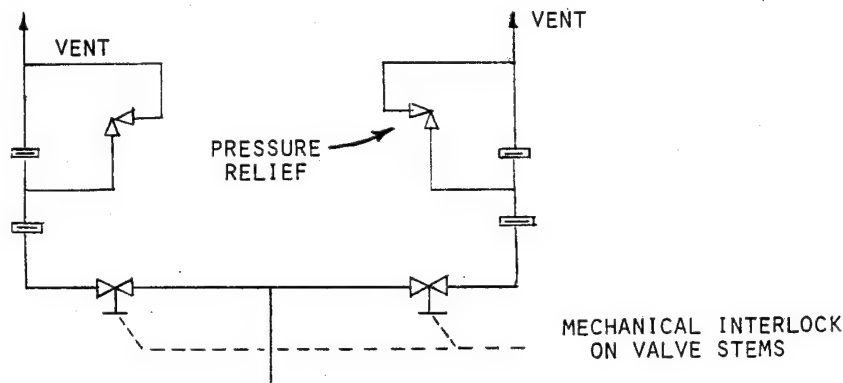
#### VCM Recovery Operation--

The VCM from the autoclave is passed directly to a water-cooled condenser until the VCM pressure drops to about 40 psi. The remaining VCM is compressed and passed to the same-water cooled condenser. The condensed VCM drains to a holding tank. The vapors leaving the condenser flow into a refrigerated condenser, where additional VCM is condensed and transferred to the holding tank. The non-condensable gases from the refrigerated heat exchanger are vented to a stack.

In addition, the recovery system is segregated from the process building and is open to the atmosphere. Hence, any VCM leaks will quickly dissipate, thus avoiding a buildup in concentration.

#### Prepolymerizer and Autoclave Rupture Discs--

Two sets of rupture discs are employed on each prepolymerizer and autoclave as shown below to minimize the down time in the event safe pressures are exceeded.



Each set consists of two rupture discs in series with a by-pass line coming out of the space between the two discs and a small relief valve that can discharge to a point downstream if the upper disc blows. This disc arrangement was devised to compensate for problems caused by persistent pin hole corrosion in the lower rupture discs. Substitution of available materials of construction did not eliminate the pin hole corrosion of the discs. The leaks created a condition which could have allowed the reactor pressure to go well beyond the safe working pressure; i.e., a leak would gradually allow the pressure across the lower disc to equalize. The autoclave pressure could then rise to twice the blow out pressure of the disc. The 10 psi relief valve by-pass prevents this condition from occurring and thus eliminates the potential for a catastrophic exposure caused by vessel rupture.

The valves preceding the discs are interlocked to assure positive engagement of the new rupture disc when the valve ahead of the ruptured disc is closed.

#### Vent Valves on VCM Lines--

When blind flanges (which are used to totally block fluid flow) are changed, there is risk of liquid VCM being released if any of the valves connected to the pipeline happen to develop leaks. Vent valves were installed on all VCM supply lines to vent any VCM that could accumulate prior to or during maintenance of spectacle valves.

#### VCM Car Unloader--

Flexible unloading lines which were clumsy and heavy were replaced by pipe assemblies employing swivel joints and valve-to-valve coupling. This approach made the unloading task physically easier and reduced the quantity of VCM that is vented to the air.

#### Vent Stack Location--

All process vents and exhausts are manifolded into a large stack. This stack extends horizontally to an open field some distance from the process building. The stack outlet is sufficiently elevated and is located downwind (relative to prevailing wind direction) of the plant area. This arrangement prevents exhausted or vented VCM from re-entering plant areas.

## Work Practices

### Warning Light System--

Each prepolymerizer and autoclave has a warning light system to warn the operator of possible error and thus reduce VCM emissions. When the light is red, vessel manways cannot be opened, spectacle valves cannot be changed and degassing filter spool pieces cannot be removed. A green light indicates that there is no pressure on the system and lines or vessels are clear of VCM.

### Housekeeping--

PVC crust and residual powder cleaned from the autoclaves were previously put into a drum which was usually left in the reactor area. It was common to record VCM levels greater than 100 ppm in areas around the drum. This problem was alleviated by insisting that employees move the scrap outdoors immediately after the autoclave has been cleaned. This example illustrates the importance of good housekeeping, which is well recognized by plant personnel responsible for reducing VCM exposure levels. For this purpose, there are two full-time employees whose sole responsibility is assuring good housekeeping in the reaction and resin classification areas.

### Standard Operating Procedures--

Any operation performed in the reaction area is covered step by step on a check list. Each step has to be signed off and the critical steps have to be double-checked and signed. For example, any spectacle valve change is a two-person operation; i.e., one operator will change it and one will verify that it has been changed.

### Leak Detection and Prevention--

The process modifications and work practices described above preclude a consistent escape of VCM from any one source. The major remaining exposure sources are intermittent leaks from valves, flanges and compressor, pump and agitator seals.

Rapid leak detection and containment is an integral part of the VCM control program. The detection system consists of two phases:

Process gas chromatograph monitoring system-- A network of small diameter tubing transports air samples from strategically located points to a sample conditioner portion of the gas chromatographic system. The same conditioner is programmed to sample each of the points every few minutes and deliver individual air samples to the gas chromatograph for analysis. Individual readings greater than 5 ppm activate a flashing red light and an audio alarm. Respiratory protection and leak detection procedures are immediately initiated when the alarm is triggered.

Leak detection procedures-- When an alarm is activated, a designated employee goes to the display panel and determines which sample point recorded excessive VCM levels. The operator then takes a portable hydrocarbon detector to locate the leak. If the leak cannot be stopped or promptly repaired, flexible exhaust hoses are positioned to remove the escaping VCM until maintenance personnel can correct the problem.

There is also a "before the fact" type leak detection procedure for all prepolymerizers and autoclaves. Obviously, it is beneficial to be able to detect

leaks from these vessels before they are charged. Before each new polymerization cycle is started, a vacuum of 2.1 psi is pulled on the vessels and held for five minutes. The process cannot proceed without maintenance if the vessel loses more than 0.1 psi.

#### Important Equipment Features

The following equipment features reduce leak occurrence and result in a reduced potential for worker exposures.

##### Valves--

FWI eccentric plug valves have replaced all Pacific ball valves. Plant engineering and maintenance personnel believe that historical data indicates that FWI valves are the best for VCM service at this plant.

Automatic blind valves manufactured by the Hilton Valve Company have been installed on several prepolymerizer lines. If the field tests continue to be successful, the valves will replace all manual blind valves. Then employees will not have to manually change these valves and exposure will be substantially reduced. The present manual blind valves will be retained as a back-up. A double block and bleed system with Hills McKenna butterfly valves also worked well. However, workers did not accept the system because they could not readily determine if the valve was open or closed.

##### Agitator Shaft Seals--

Both ends of the autoclave have packed seals with grease maintained at 300 to 400 psi. A patent is pending for a sensing system that determines when excessive grease is used and, therefore, when maintenance is required.

The prepolymerizer agitator has double mechanical seals pressurized with mineral oil. These seals last one to two years without requiring maintenance. However, the preventive maintenance programs dictate that they be changed at the first of each year.

##### Recovery Compressor--

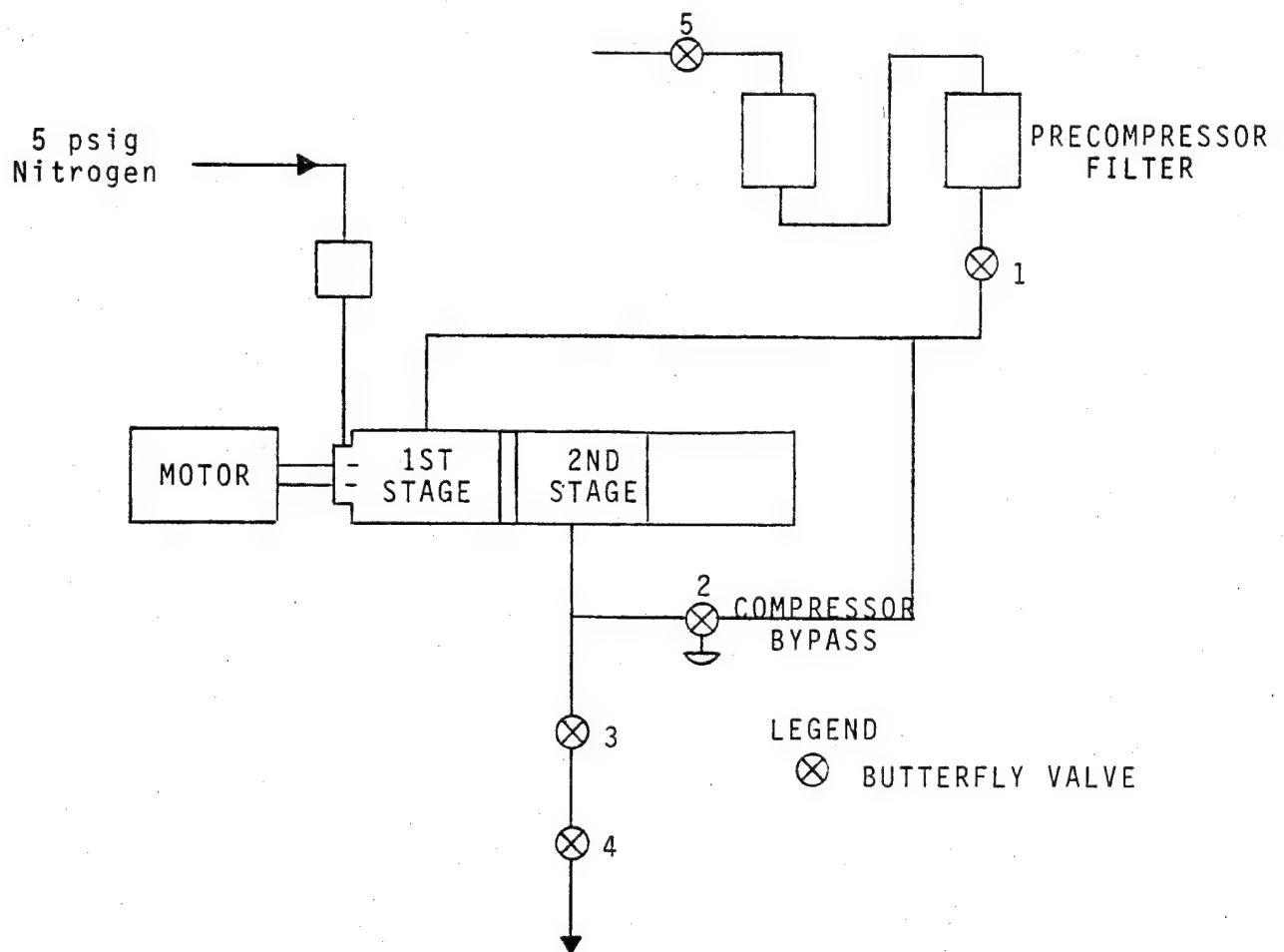
This compressor was a large source of VCM escape (refer to Figure A.2-2). When the compressor was down (and before automatic valve 3 was installed), VCM would be forced by pressure differential from the recovery system back into the second stage of the compressor. From here it would pass through the first stage, into the crankcase, and finally into the workplace. To alleviate this problem: 1) automatic inlet and exit block valves were installed and are closed as soon as the compressor stops (this prevents VCM from bleeding back into the compressor); 2) double mechanical seals were installed on the shaft where it comes out of the crankcase; and, 3) inflatable rubber donuts encased in spool pieces were installed on the shaft just before it enters the crankcase.

The mechanical seals are pressurized with nitrogen during operation to prevent leakage to the work area. If a seal failure occurs on the seal in contact with the process stream, the nitrogen will leak into the process stream.

##### Pumps--

Pumps used for transporting VCM or process streams containing VCM are located outdoors. The pumps are equipped with double mechanical seals with





Operation sequence:

- When compressor starts, valves 1, 2, 3 and 5 are open and system recirculates for 30 seconds.
- Valve 2 is closed.
- When the compressor stops, valves 3 and 1 close and valve 2 opens.

Figure A.2-2. Vent Compress System (Wharton Compressor)

pressurized water/glycol solutions between the seals.

#### Autoclave leaks--

Periodically, leaks develop in welds on the agitator shafts. Since the autoclave pressure is much greater than the water pressure in the shaft, VCM leaks into the water. Until the welds can be permanently repaired, maintenance personnel use epoxy as a patching material. A vented air eliminator is used to concentrate and remove the VCM from the water that is used to pressurize the seal. The VCM released is vented to a stack. Any VCM dissolved in the water in the seal would be released when the reactor jackets are heated at the onset of the reaction.

The seals which have performed satisfactorily in equipment handling VCM are tabulated in Table A.2-1.

TABLE A.2-1. Seals for Compressors, Pumps and Agitators

<u>Application</u>	<u>Supplier</u>	<u>Seal Description</u>
PREPO Drain Valve	Pechiney-St. Gobain	Plunger type valve located on bottom of vessel. Opens and closes inside Prepo vessel. Adjustable seat ring prevents leaks. Hydraulically operated with 2000 psi oil pressure.
POPO Agitator Seal	Pechiney-St. Gobain Chempro	Double mechanical seal. French design parts Teflon dipped.
PREPO Agitator Seals 4½ inch shaft	Crane	Type 9T double mechanical seals pressurized with oil.
Pumps handling VCM	Sealol	Bellows type seal Type 670 Hastelloy B.
Compressor		
Vacuum Pump	Chesterton	Double mechanical seal pressurized with nitrogen.
VCM Line Valves	FWI	Eccentric plug valves.

#### Local Exhaust Ventilation System

The local exhaust ventilation system for the reaction area consists of a series of 12-inch diameter, free hanging flexible ducts positioned as indicated in Figure A.2-3.

The system consists of 14 flexible ducts with a total design airflow of 3.30 m<sup>3</sup>/s (7000 cfm). The ducts provide at least three functions:

- (1) Fresh air circulation and exhaust for the prepolymerizers and autoclaves when the manways are opened

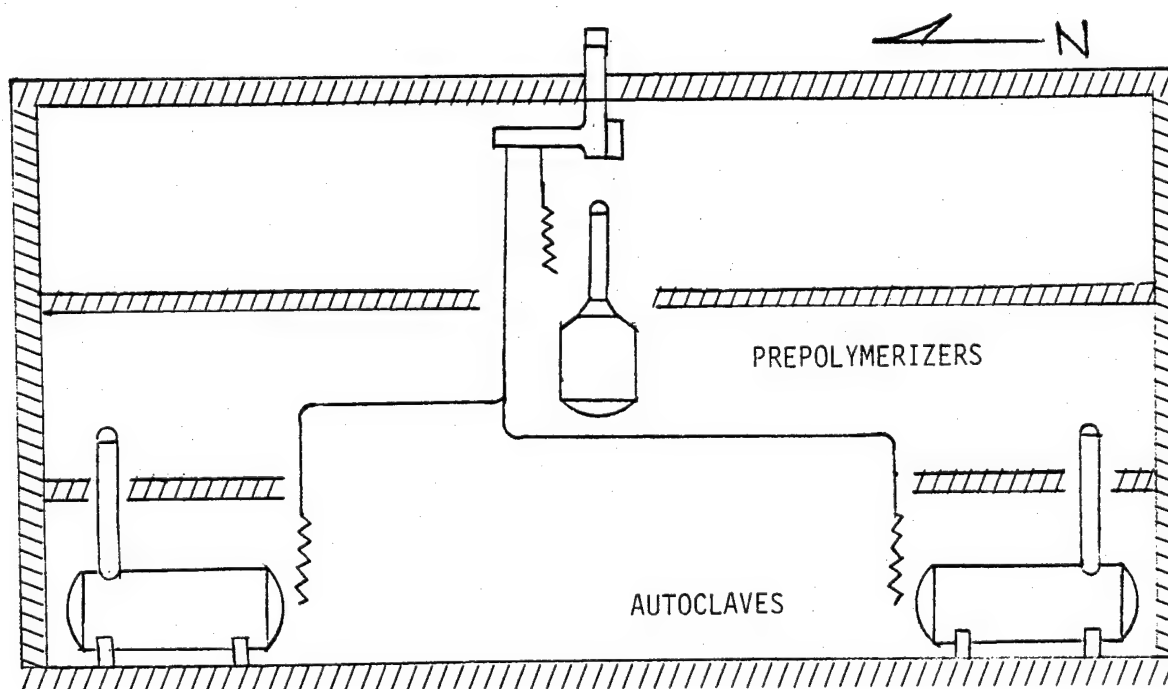
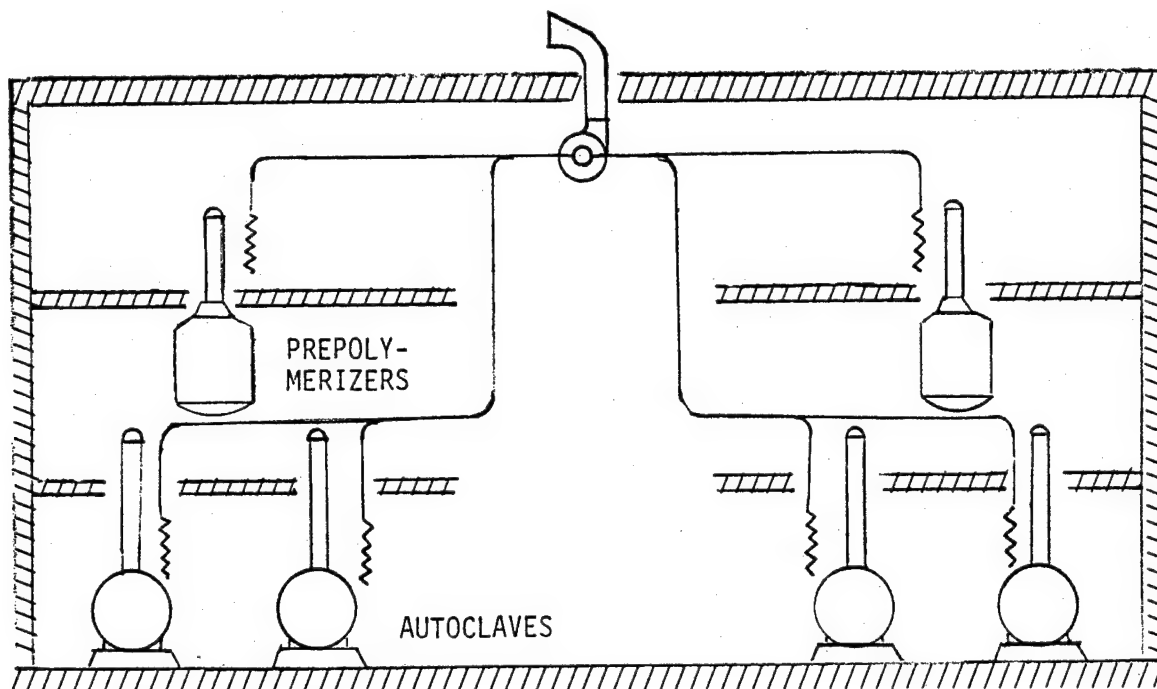
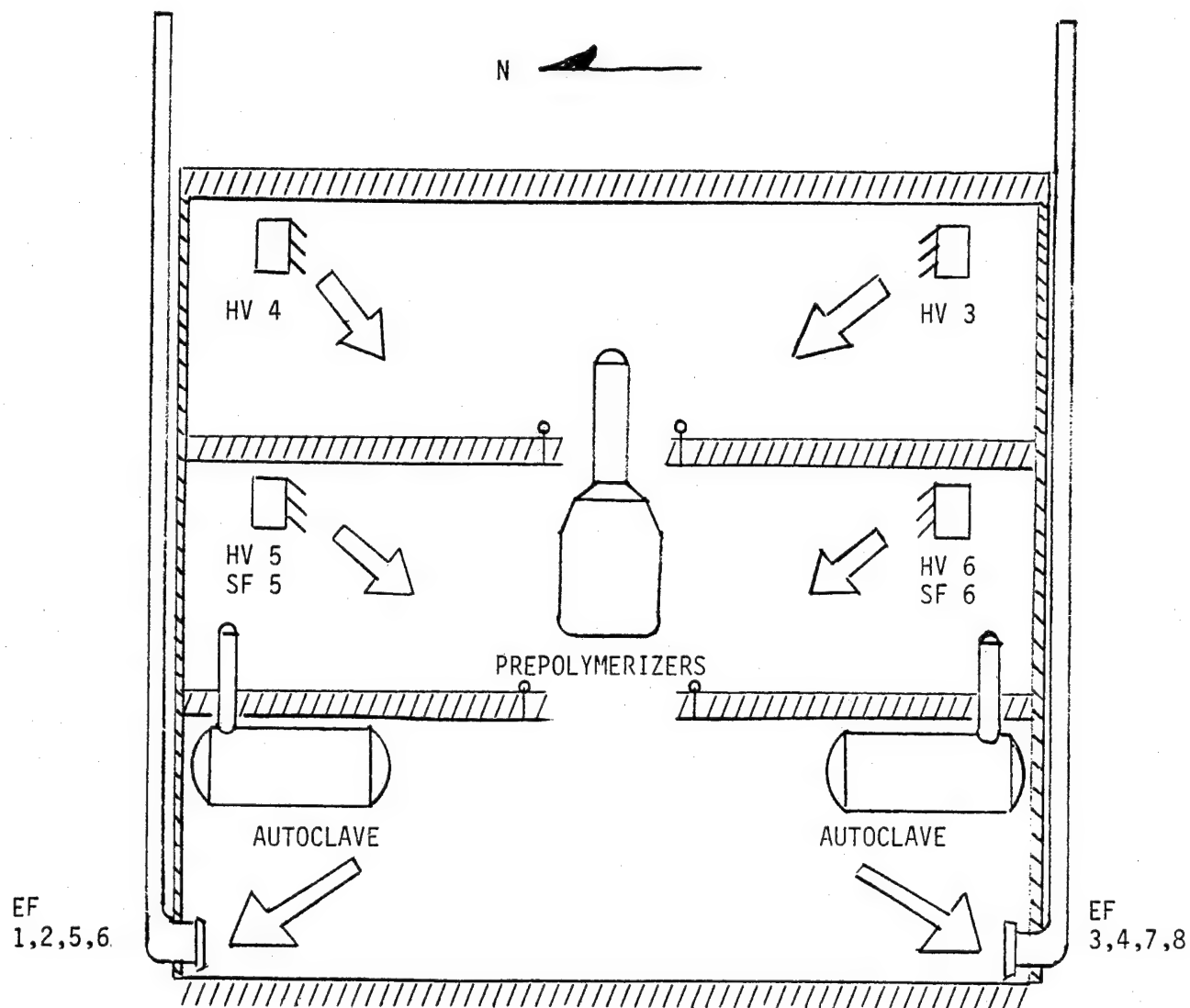


Figure A.2-3. Local Exhaust System



	Fan	Normal, m <sup>3</sup> /s	Emergency, m <sup>3</sup> /s
EXHAUST	EF 1	4.72	4.72
	EF 2	4.72	4.72
	EF 3	4.72	4.72
	EF 4	4.72	4.72
	EF 5	0	3.78
	EF 6	0	3.78
	EF 7	0	3.78
	EF 8	0	3.78
	Local exhaust	10.0	10.0
	Filter/compressor room	10.4	10.4
		<u>39.3</u>	<u>54.4</u>
SUPPLY	SF 5	0	6.61
	SF 6	0	6.61
	HV 3	5.29	5.29
	HV 4	9.44	9.44
	HV 5	12.3	12.3
	HV 6	12.3	12.3
		<u>39.3</u>	<u>52.5</u>
Air changes/hour		28.4	39.3

Figure A.2-4. General Ventilation System

- (2) VCM containment during maintenance operations or periodic functions, such as changing the spectacle valves
- (3) Containment of VCM from intermittent leak sources, such as valves, flanges or agitator seals

When any of the flexible ducts are not needed for these purposes, they are dampered and thus do not exhaust any air. The design airflow for each duct ranges from a minimum of  $.236 \text{ m}^3/\text{s}$  (500 cfm) [all open] to a theoretical [never occurs] maximum of  $3.30 \text{ m}^3/\text{s}$  (7000 cfm) if all except one duct is dampered. However, it is probably a good approximation to assume an average duct airflow of  $.472 \text{ m}^3/\text{s}$  (1000 cfm).

The efficacy of the system lies in its flexibility. There are no constant sources of VCM escape into the workplace and only two predictable sources: 1) opening prepolymerizer and autoclave manways at the end of each cycle, and 2) maintenance operations, particularly involved with the spectacle valves. Other potential sources of exposure (i.e., intermittent leaks) are not predictable, and must be located and temporarily contained until repairs are effected. Obviously, a permanent exhaust hood could not be provided at every process point where leaks are possible. The only viable alternative is a flexible duct system, such that one duct can provide exhaust as necessary for a large number of potential leak points.

The filter and compressor room is open to the first floor of the reaction area. Each of the four large vent compressors is provided with an exhausted chamber around the seal area. Eight filters are located along two opposite walls. Directly behind each filter is a floor-mounted, plain face exhaust duct with an average airflow of approximately  $.472 \text{ m}^3/\text{s}$  (1000 cfm). These exhausts are the sole source of general exhaust ventilation for the room. They also serve the purpose of VCM containment when a filter develops a leak or when filter elements are being cleaned or changed. Prior to process modifications to the compressors and the installation of the exhaust systems, this room was a major source of VCM escape to the rest of the plant area. However, since there is no forced supply air into the filter and compressor room,  $\sim 7.6 \text{ m}^3/\text{s}$  ( $\sim 16,000$  cfm) exhausted, the room is at lower atmospheric pressure than the reaction area. Thus, VCM escape from the compressors or filters will not travel into the reaction area and increase employee exposure.

#### General Exhaust Ventilation System

The general exhaust ventilation system is schematically depicted in Figure A.2-4.

In normal conditions, there is  $39.3 \text{ m}^3/\text{s}$  (83,200 cfm) exhaust and an equal volume of supply air (tempered in the winter), or approximately 28 room air changes per hour. In emergency conditions, the system will exhaust  $54.4 \text{ m}^3/\text{s}$  (115,200 cfm) and supply  $52.5 \text{ m}^3/\text{s}$  (83,200 cfm) tempered air in winter. This yields an emergency flow rate of approximately 39 room air changes per hour. These very high rates of air movement provide an extensive dilution of VCM contaminated air and minimize the frequency and duration of VCM excursions over 5 ppm.

The floors are arranged as open-grate mezzanines such that the downward

airflow profile is not impeded. It is probable that the exhaust outlets were positioned at ground level to assist VCM removal during large spills or leaks (i.e., VCM is much heavier than air and would tend to sink and concentrate at the lowest levels). Two-thirds of the process equipment (8 autoclaves) is located on the first floor, with the rest (4 polymerizers) located on the second floor. Hence, the areas with the greatest potential for leakage are located closest to the exhaust outlets, and the process area that a given leak would contaminate is minimized. The only potential problem with this system design is the possibility of stagnation points (dead air spaces) where VCM concentrations could accumulate over time. These could be anticipated down the middle (east west axis) of the first and third floors, and at the north and south walls on the second floor. However, the plant has not experienced this phenomenon, probably due to the large volumes of air exchanged and good mixing due to the location of the local exhaust ducts on the first and second floors.

#### EXPOSURE DATA AND CONCLUSIONS

An extensive VCM monitoring program was initiated in 1974 using charcoal tube samples worn full-shift by exposed employees. Perhaps the best method of illustrating the effect of the control measures described in this study is to compare employee TWA exposures measured during late 1974 and early 1975 with recently collected sample data (see Table A.2-2).

Table A.2-2. Comparison of Employee Exposure Data\*

Job Function	No. of Samples	Sample Period	Average TWA Exposure	January, 1977	
				No. of Samples	Average TWA Exposure
Supervisor	13	10/74-3/75	9.8 ppm	3	1.1 ppm
Foreman	15	10/74-5/75	7.7 ppm	4	0.8 ppm
Control Room Operator	9	10/74-3/75	6.0 ppm	4	0.7 ppm
Field Man	11	11/74-5/75	2.7 ppm	4	0.3 ppm
Crew Leader	13	11/74-3/75	7.5 ppm	3	0.6 ppm
Asst. Crewleader	17	10/74-2/75	7.0 ppm	7	0.9 ppm
Autoclave Cleaner	19	10/74-1/75	5.9 ppm	10	3.3 ppm (due to one very high level)
Floorman	12	10/74-4/75	5.0 ppm	4	0.3 ppm
Maintenance Man	12	10/74-2/75	4.0 ppm	9	0.6 ppm
Engineers	9	10/74-2/75	3.8 ppm	-	-
Compound Plant Employees	16	1/75-3/75	2.2 ppm	4	0.3 ppm

\* Employees wear approved respirators during all functions where vinyl chloride exposure is possible. These readings were taken while respirators were worn, and do not represent the levels in the air the employees were breathing.

## PERSONAL PROTECTIVE EQUIPMENT FOR VCM

Employees who work or enter areas regulated for VCM exposure use one of several types of respirators based on the VCM concentration and the specific nature of the job function. The key to the respirator program is the process gas chromatograph monitoring system. When VCM concentrations in any area exceed 5 ppm, a flashing red light is activated and all employees in the area are required to wear a Type C, continuous flow, full or half-face piece respirator or a powered air purifier with full or half-face mask.

To supplement the area monitoring system relative to respirator usage, an evaluation was made to determine job functions suspected of releasing VCM in excess of 1 ppm. Eighteen job functions were identified for which Type C supplied air respirators are required for the duration of each operation.

Employees are issued a clean set of work clothes each day. Daily showers are encouraged, but not required. Vessel cleaning employees are required to use hard hats, safety goggles and gloves in addition to the Type C supplied air respirators.

## PLANNED OR ONGOING IMPROVEMENTS

The VCM control program is continually being improved and refined to further reduce worker and environmental exposure. Present engineering projects include:

- The installation of a treatment system for reducing VCM concentrations in vented or exhausted air to less than 10 ppm. This is directed primarily towards reducing emissions in compliance with newly promulgated EPA regulations for vinyl chloride.
- The installation of a series of 1½" and 2" exhaust pipes leading from the following process points to the existing local exhaust main:
  - Autoclave manual vent valves
  - Monomer charge valves
  - Vacuum leak valves
  - Compressor crankcase vents

This system is planned as an adjunct to the existing local exhaust system. It is anticipated that a booster exhaust blower of 6.14 m³/s (13,000 cfm) capacity will be required. Most of these exhaust points will be "dead-headed" when the valves are closed. For example, the system will induce a negative pressure on the autoclaves when the vent valves are opened prior to opening the vessel. Or the pipe space between the monomer charge valve and the spectacle valve will be evacuated when the latter is opened to insert or pull out the spool piece. Hence, before any process equipment is opened or entered for cleaning, maintenance or valve changing, the VCM contaminated air space will first be evacuated and maintained under negative pressure.

- The development of a prepolymerizer charging sequence modification to reduce crusting on the vessel interior surfaces. The present operating

procedure involves charging the vessel above the reaction weight and degassing excess monomer off until the desired weight is reached. This sweeps out oxygen and volatile material which acts to inhibit the reaction. Sequence changes are being contemplated for the purpose of keeping the inhibitors in the vessel during heatup, thus slowing down the reaction and reducing crust buildup.

- Research correlating the amount of crust with certain impurities in the feedstock VCM. This study may enable a future reduction in crusting if the important impurities can be isolated and removed prior to polymerization.
- The installation of a rapid opening discharge port system for the autoclaves. This will reduce the exposure to the worker who currently must manually remove 12 bolts on the port flange, remove the plug and insert the spool piece.

#### CONTROL OF OTHER POTENTIAL HAZARDS

##### PVC Dust

The PVC resin classification system is totally enclosed, therefore, it is not a large source of PVC dust exposure. However, leaks could occur from resin hoppers, conveyance systems, screeners or crushers. Leakage is not a problem at this plant primarily due to a dust collection system, which induces a negative pressure on the classification equipment. Connections between equipment are maintained tight and good housekeeping is provided using an industrial grade vacuum cleaner. Further, employees are rarely required to enter the classification area, so the possible exposure time is limited.

##### Noise

Noise levels range from 85 - 88 dBA in all process areas. Since this level is within the OSHA limit of 90 dBA and most employees spend a significant amount of time in the closed control room (essentially no noise exposure), it is concluded that noise is not a significant exposure for this process according to OSHA standards.



### APPENDIX A.3. PVC SUSPENSION PROCESS - CASE STUDY NO. 3

#### PROCESS SUMMARY

A simplified process flow diagram for a suspension process used to manufacture polyvinyl chloride is presented in Figure A.3-1.

The reactors are operated in parallel and out of phase to supply a continuous feed of PVC to subsequent parts of the process. The cycle begins with the addition of water to an empty reactor. Next, dry ingredients are dropped into the reactor through the open manway. Once the manway is closed and sealed, the vinyl chloride monomer is pumped into the reactor from a nearby weigh tank. During the polymerization cycle, the heat of reaction is removed through external cooling jackets.

At the end of the reaction, the slurry is dropped into a stripping vessel, where unreacted VCM is removed and subsequently recovered. During this period, a vacuum is also pulled on the reactor to remove residual VCM.

The slurry is pumped from the stripper to an agitated blend tank where different batches are mixed to achieve a uniform product consistency. The blended slurry is pumped to a centrifuge that separates the water from the PVC particles. The wet PVC cake is transferred to a rotary dryer where any remaining moisture is vaporized under heat and vacuum.

The dry PVC particles are pneumatically conveyed to a product storage bin for bulk transport, bagging, or used as feed stock in the compounding plant.

#### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

##### Vinyl Chloride

TWA 1 ppm  
Ceiling limit 5 ppm for any 15-minute period

##### Polyvinyl Chloride Dust

TWA 15 mg/m<sup>3</sup> total dust

##### Noise

TWA 90 dBA

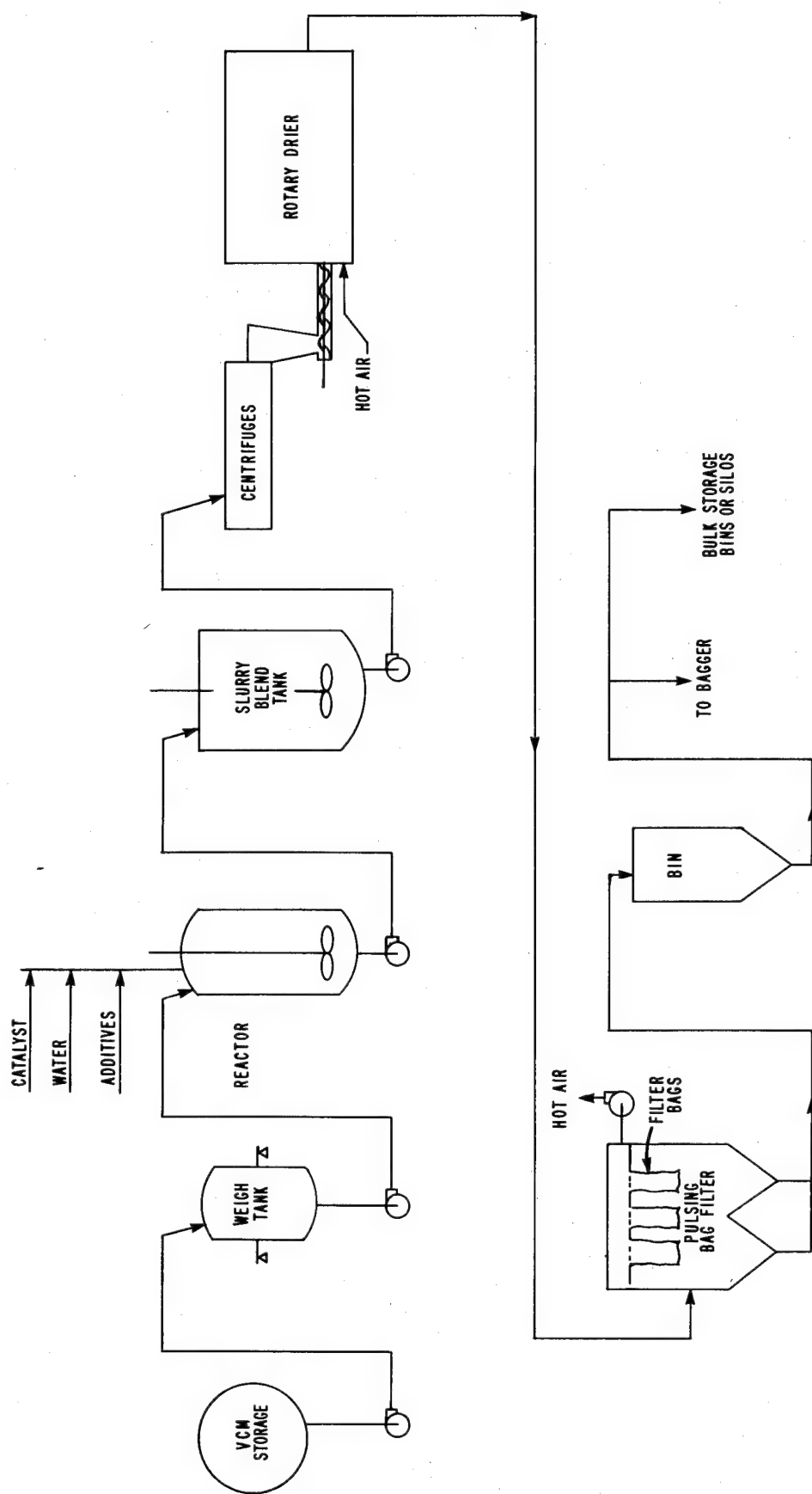


Figure A.3-1. PVC Suspension Process

## CONTROL TECHNIQUES

### Process Design, Modification and Maintenance

#### Stripping Operation--

The most effective process modification to date is the installation of a stripping operation to remove and subsequently recover residual vinyl chloride from the PVC slurry in the stripping tank and from the vapor space in the reactor. Once the PVC slurry has been dumped from the reactor into the stripping tank, the recovery compressors draw vacuum on both vessels. The compressors are arranged in a two-stage operation with an intermediate heat exchanger between the first and second stages. A heat exchanger following the second compressor condenses the vinyl chloride at about 80 psi pressure. The condensed vinyl chloride is pumped to an accumulator and transferred to master mix tanks for future use. The inert gas accumulated in the system must be vented to the atmosphere following the final condenser stage after the second compressor. A refrigerated heat exchanger is used to reduce trace levels of vinyl chloride in the off gas to acceptable standards as specified by the Environmental Protection Agency (EPA). During each shift, the system must be purged of accumulated water, which varies in quantity from a pint to a couple of gallons per shift to avoid damage to compressor heads.

The stripping operation reduces exposure in two ways: 1) residual vinyl chloride in the PVC slurry is substantially reduced (although measurements of vinyl chloride concentrations in the stripped slurry were not available, still the levels are believed to be sufficiently low to prevent further exposure downstream of the operation), and 2) vinyl chloride in the empty reactor vapor space is removed to the degree that the vessel may be opened following the polymerization cycle without causing a significant release of vinyl chloride into the workplace.

#### Vinyl Chloride Weigh Scales--

Periodic leaks have occurred from the weigh scale relief line flanges and the rupture disc holders. Both were changed from 120 psi flat face to 150 psi raised face connections to reduce leakage. The raised flange is a male/female arrangement providing a smaller and more secure gasket contact area and, hence, a better seal. In addition, the male mating surface consists of a continuous spiral groove that prevents the direct passage of vinyl chloride to the workplace in the event of a leak. The modifications have been very successful.

#### Waste Water Vapor Containment System--

There are various process waste water streams containing small quantities of vinyl chloride that must be discharged. In order to eliminate these as a source of vinyl chloride escape to the workplace, it is necessary to remove the vinyl chloride from these streams prior to discharge into the sump. A blend tank was modified to receive the liquid streams from:

- Blow downs from both compressor separators
- Recovered vinyl chloride filter drains
- Knockout pot drains
- Water drain from pure vinyl chloride weigh tank, recovered vinyl chloride

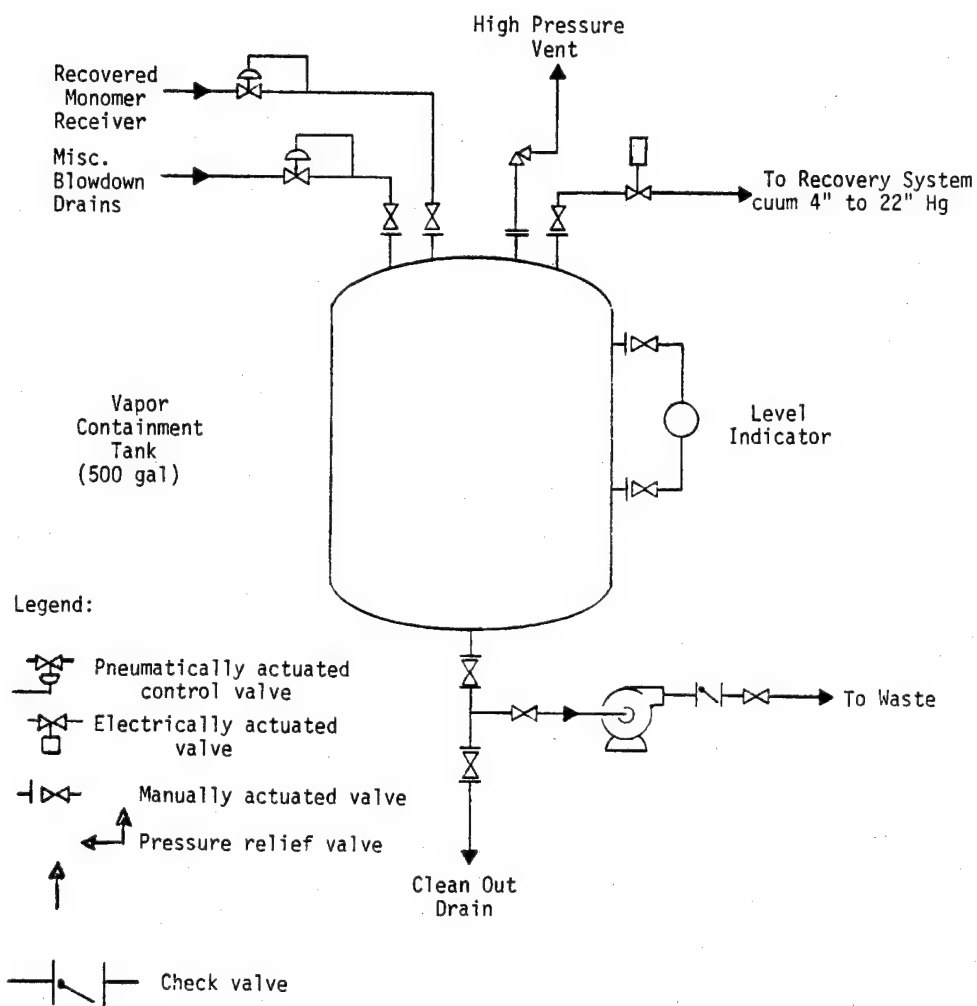


Figure A.3-2. Waste Water Vapor Containment System

storage tank and master mix tanks

- Water drain from recovered vinyl chloride receivers
- Drains from all charge filters

The tank is equipped with a relief valve set at 150 psi and pressure control devices to maintain vacuum at all times. The vacuum is applied via the vapor line connection (refer to Figure A.3-2) to the inlet of the recovery system and varies from a maximum of 22 inches high at no load to as low as 4 inches high at maximum vapor loads. Heat for the operation is supplied solely by the sensible heat in the inlet water, which enters at approximately 100° to 120° F. The vinyl chloride recovered in the containment system is transferred to the vinyl chloride recovery system.

#### Cuno Filters--

Piping modifications were made to all cuno cartridge filters such that they may be drained and flushed with water before opening for cleaning. Although employees must still wear respiratory protection during the cleaning operation, vinyl chloride escape is substantially reduced. Filter opening and cleaning no longer causes high vinyl chloride concentrations in areas remote to the filters.

The slurry strainers downstream of the stripping operation also have to be periodically opened and cleaned. This procedure is no longer a source of employee exposure and workplace contamination because of the effectiveness of the slurry stripping operation.

#### Blend Tanks--

Prior to the installation of the stripping operation, the blend tanks were major sources of VCM escape. The tops of all tanks were sealed; weight was added to the manway covers to provide better seals and agitator shaft seals were installed. The vent line dampers were permanently affixed in the open position to assist the outflow of vinyl chloride and to avoid pressure buildup in the tanks. Although these controls are no longer crucial since the advent of the stripping operation, they illustrate simple measures that can be implemented to eliminate a serious source of employee exposure.

### LEAK DETECTION AND PREVENTION

#### Leak Detection

Plant engineers involved in the vinyl chloride control program consider rapid leak detection the most important control technique other than the stripping process. On a regular schedule, an employee uses a portable hydrocarbon detector to check all potential leak sources. VCM leaks can thus be detected early when they are small and the resulting exposure area is not extensive. Many leaks are detected and repaired or contained well before the automatic monitoring system would be alerted. Work orders resulting from the search and secure program carry priority status. Each month, these records are analyzed and summarized by top management and either new control goals are established or ongoing ones are followed up.

A process gas chromatograph system was installed to alert employees to

excessive levels of VCM and to allow location and repair of VCM leaks. There are 15 permanent sampling points in process areas selected for their high leak potential. The monitoring cycle is 1½ minute per sample point; i.e., a sample is repeated at each point every 23 minutes. However, since many of the sample points are in the same relative area, it is unlikely that a significant leak could go undetected for 23 minutes during the cycle. The system analyzer activates alarm lights in the work area when a VCM excursion exceeds 5 ppm. When the alarm light is activated, the affected workers must leave the work area or put on air line respirators.

#### Important Equipment Features

The existing double mechanical seals on all pumps and compressors handling fluids containing VCM have been converted to Chesterton Company self-aligning double mechanical seals, Model No. 241. A mixture of 6% glycerine and 40% water is used to pressurize the seal. The glycerine serves as a lubricant and prevents freezing during cold weather.

#### LOCAL EXHAUST VENTILATION SYSTEM

##### Pump and Compressor Floor

Attempts to eliminate vinyl chloride leaks from pumps and compressors with different types of seals have not been altogether successful. Plant personnel have found it necessary to supply local exhaust ventilation as an adjunct to the ongoing experiments with seals. Since the ultimate future control philosophy rests with leak-proof seals, with flexible hose, the plant operators are temporarily relying primarily on portable air blowers (each rated at 0.80 m<sup>3</sup>/s (1700 cfm)) to exhaust VCM from process leaks.

Each compressor drive shaft is enclosed and exhausted with each air blower providing suction off two compressor shafts. Hence, each compressor has an average airflow of 0.40 m<sup>3</sup>/s (850 cfm).

The VCM charge pumps are also exhausted via an 8-inch flexible hose positioned as close as possible to the pump seals. Velometer measurements resulted in average capture velocities of 2.03 m/s (400 fpm) at the farthest edge of the seals.

There is also an auxiliary air blower which is used only during maintenance operations. Employees may position the flexible exhaust duct as needed depending on the particular operation and the location of the potential escape of vinyl chloride.

As temporary control measure, the system is relatively effective. The only drawback is the lack of facilities for dispersing exhausted vapors away from the building such that re-entry is not a problem. At present the flexible exhaust ducts (on the positive side of the air blowers) are fastened to the grill covering the general exhaust fans. In other words, the ducts are discharged to an area where the exhausted contaminants may be entrained in the general exhaust flow to the exterior of the building.

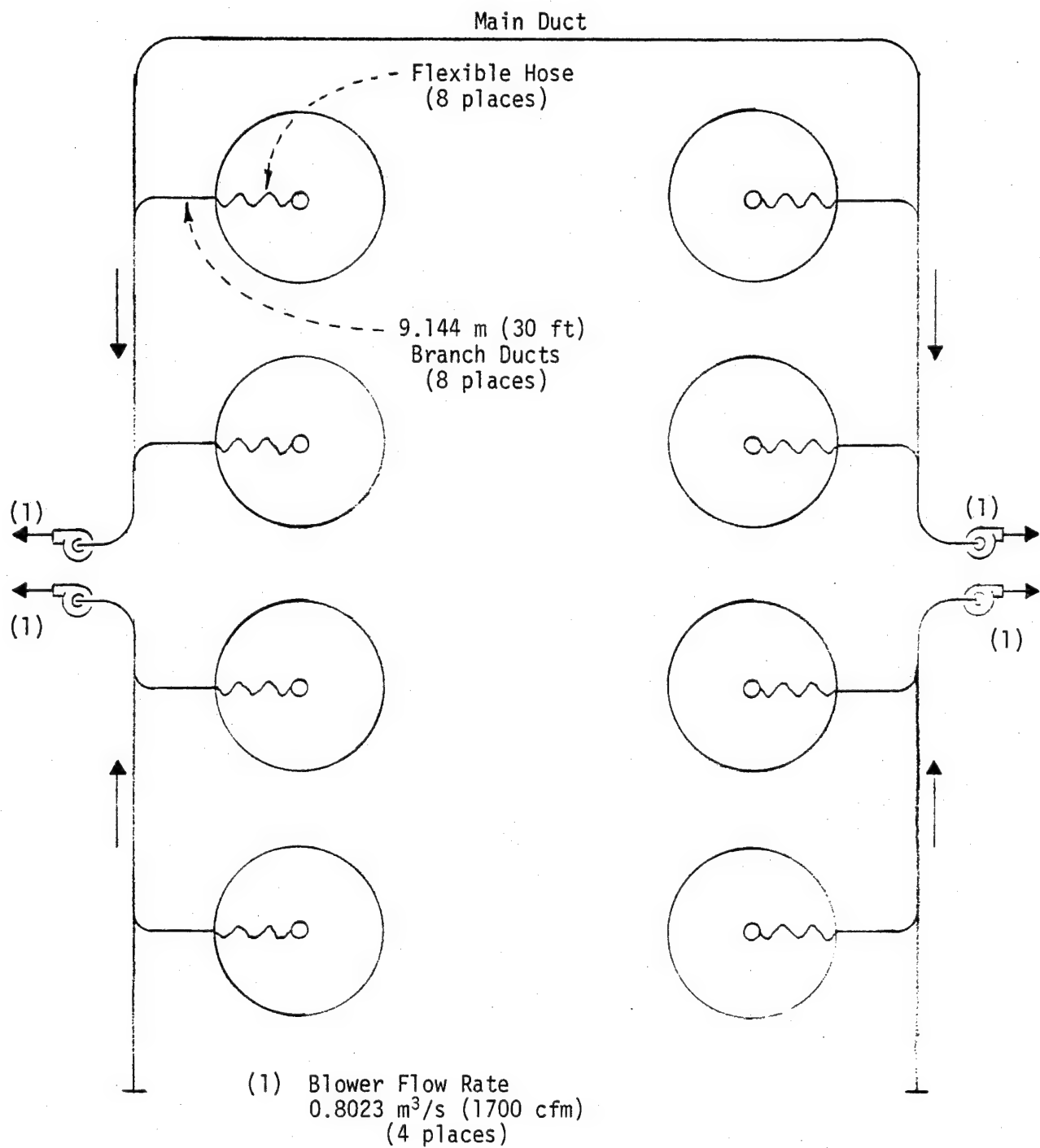


Figure A.3-3. Local Exhaust System for Reactor Floor Area (TOP VIEW)

## Reactor Floor

The local exhaust system for the reactor floor is permanently installed as depicted in Figure A.3-3.

Each reactor top is equipped with a 30-foot flexible exhaust hose, rated at a minimum of  $0.40 \text{ m}^3/\text{s}$  (850 cfm) when all branches are opened. However, each flexible hose is dampered such that when exhaust is not needed in a given area, it can be closed and the additional airflow diverted to the open branches.

The primary purpose of the system is to provide exhaust when the reactors are opened for cleaning and/or charging. The flexible duct is inserted into the manway as soon as it is opened. (Operators wear air respirators during the short time between when the manway is opened and the flexible exhaust hose is inserted.) When the reactor is closed during the polymerization cycle, the flexible duct will either be dampered or positioned to contain a vinyl chloride leak from process points near the top of the reactor (e.g., manway gas-kets, vinyl chloride header, etc.).

## GENERAL VENTILATION SYSTEM

### Pump and Compressor Floor

Engineering blueprints were not available for the general exhaust system in this area. Two sets of propeller-type exhaust fans are located on each of three sides of the building. This includes the emergency exhaust fans which are automatically activated if the monitoring system picks up a vinyl chloride level in excess of 50% lower explosive level (LEL). The outlet velocity profiles for the exhaust grills were highly variable, and thus it was virtually impossible to estimate the exhaust airflow and corresponding air change rate for the area. However, it appeared to be quite high.

Mechanically forced makeup air (tempered in winter) is also supplied but again the airflow capacity could not be determined. However, since the building is under a large negative pressure, it can be assumed that the supply air does not equal the exhaust, at least during the winter.

### Reactor Floor

Under normal conditions, general ventilation on the reactor floor is provided by four roof-mounted fans rated at  $4.48 \text{ m}^3/\text{s}$  (9500 cfm) each, or a total of  $17.94 \text{ m}^3/\text{s}$  (38,000 cfm). This corresponds to a general ventilation rate of approximately 20 air changes per hour.

In emergency situations, six wall fans are activated and develop an exhaust rate double that achieved during normal conditions. The system is activated automatically based on a measured vinyl chloride concentration of 0.5 ppm and is generally operated continuously during the summer.

Mechanically forced makeup air (tempered in winter) is provided and has an airflow capacity of  $12.17 \text{ m}^3/\text{s}$  (26,000 cfm).



## PERSONAL PROTECTION EQUIPMENT

Respiratory protective equipment usage is keyed to the air monitoring (process gas chromatograph) alarm light system. When any sample head picks up a vinyl chloride concentration in excess of 5 ppm, an alarm light is activated and employees are required to wear a filter cartridge respirator or a half face Type C supplied air respirator. Certain job functions have been identified as having a potential for excessive exposure to vinyl chloride; e.g., entering reactors for cleaning, opening a reactor manway and certain maintenance operations. Respiratory protection is similarly required during these tasks.

When workers enter a vessel for cleaning, a full work uniform (including gloves, head covering and supplied air respirator) is required. Clean work uniforms are supplied to employees on a daily basis.

## EXPOSURE DATA AND CONCLUSIONS

A comprehensive air sampling program was initiated at the end of 1974. Since that time, personal samples have been collected for each exposed employee on a monthly basis. The averaged results of these samples for 1975 and 1976 are presented in Figure A.3-4 to illustrate the effectiveness of implemented engineering control measures.

The decline in average employee exposure is striking for all job classifications except bagger/reactor cleaner, which has only been reduced by about 20%. In fact, all job classifications except the bagger/reactor cleaner are well below the permissible limit of 1 ppm TWA. Air respirators are worn when entering reactors and during bagging operations.

## CONTROL TECHNIQUES FOR OTHER POTENTIAL HAZARDS

### Polyvinyl Chloride Dust

There is little opportunity for polyvinyl chloride dust to escape into the workplace except at the baggers. Although the baggers are not equipped with local ventilation, the PVC particles are relatively large, the area is periodically vacuumed and employee exposure is very slight. Full-shift personal samples for total dust produced the following data:

<u>Job Classification</u>	<u>TWA, mg/m<sup>3</sup></u>	<u>Permissible Limit, mg/m<sup>3</sup></u>
Bagger	0.126	15.0
Dryer Operator	0.208	15.0

### Noise

<u>Location</u>	<u>Sound Levels, dBA</u>	<u>Source</u>
Polymerization Building Pump and Compressor Floor	93	Pump and compressor noise; no controls observed; floor is isolated with limited employee access except for maintenance operations.

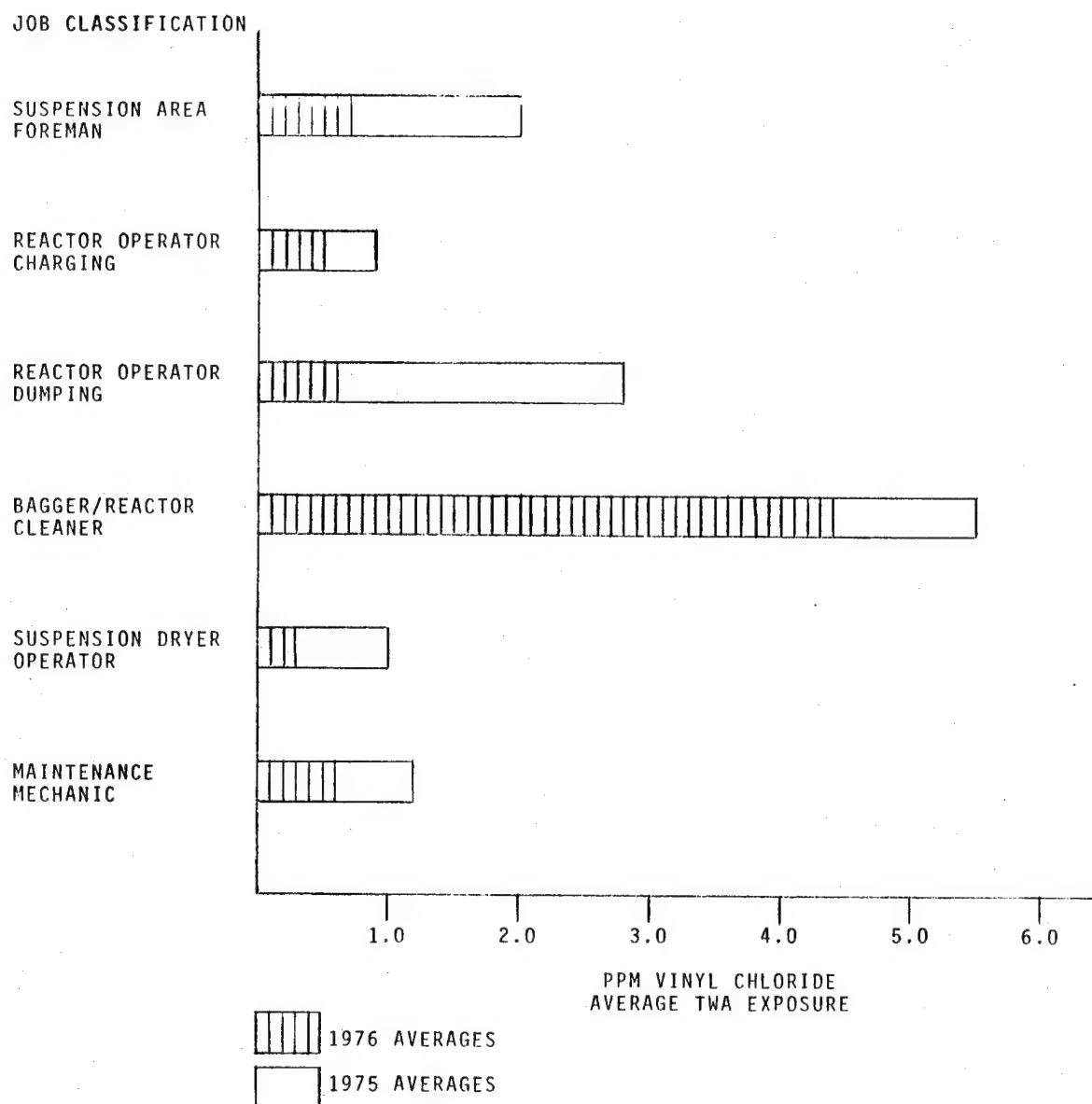


Figure A.3-4. Average Personal Sampling Results

Reactor Floor		
Control Panel	87	Predominant noise source is agitator drive gear box; no controls observed.
Middle of Aisle	91	
Opposite Agitator	95	
Drive Gear Box		
Around Centrifuge	85	Centrifuge is vibration isolated from the floor and is well encased with steel.

Noise dosimetry data collected on a reactor operator show a 70% permissible exposure relative to the standard of 90 dBA TWA. No employees in this process are required to wear hearing protection.

## APPENDIX A.4. PVC DISPERSION POLYMERIZATION PROCESS - CASE STUDY NO. 4

### PROCESS SUMMARY

A simplified flow diagram for this process is depicted in Figure A.4-1.

Batch ingredients are made up and mixed in an agitated weigh tank. Minor ingredients such as buffers and emulsifiers are dumped into the tank through an air lock zone with an exhausted feed spout. The VCM and trichloroethylene are pumped into the tank via a closed piping system.

The batch mix tank ingredients are then passed through three homogenizer pumps in series. These pumps force the batch through specially designed orifices to obtain dispersion of the liquid droplets in the water phase. A typical running time per batch is 1½ hours.

From the homogenizers, the slurry is pumped into tall, narrow reactors for the 12-hour reaction. Heat generated during the reaction is removed by a reflux coil and a jacketed vessel surface. Following the reaction, the PVC slurry is pumped to a stripper, where residual VCM is removed and recovered. During this time, the reactors are degassed and then cleaned with high pressure water.

After the stripping operation, the slurry is transferred to blend tanks, which assures uniformity of batches. At least four batches are mixed before any is pumped to the filters. A fume scrubber with a water spray knocks out any foam that may be entrained in the gas phase leaving the stripper. The filters are a rotary drum type with cloth media and a 12-foot diameter drum about 18 feet long. The wet cake is conveyed from the filter and passes through a cake breaker that breaks up large lumps.

The cake is accumulated in a wet cake bin and fed at a fixed rate into the dryer. The dryer consists of a 24-inch duct supplied with hot air from gas fired heaters. The fluidized PVC particles entering the hot airstream are dried and transported to a primary cloth collector.

The dried resin particles are collected and screw conveyed through a screen into micropulverizers operating in parallel. The PVC particle size is decreased and standardized in the micropulverizers. The resin is then air conveyed to a fine product collector, separated from the airstream and stored for future packaging as needed.

### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

#### Vinyl Chloride Monomer

TWA 1 ppm, ceiling limit 5 ppm for any 15-minute period

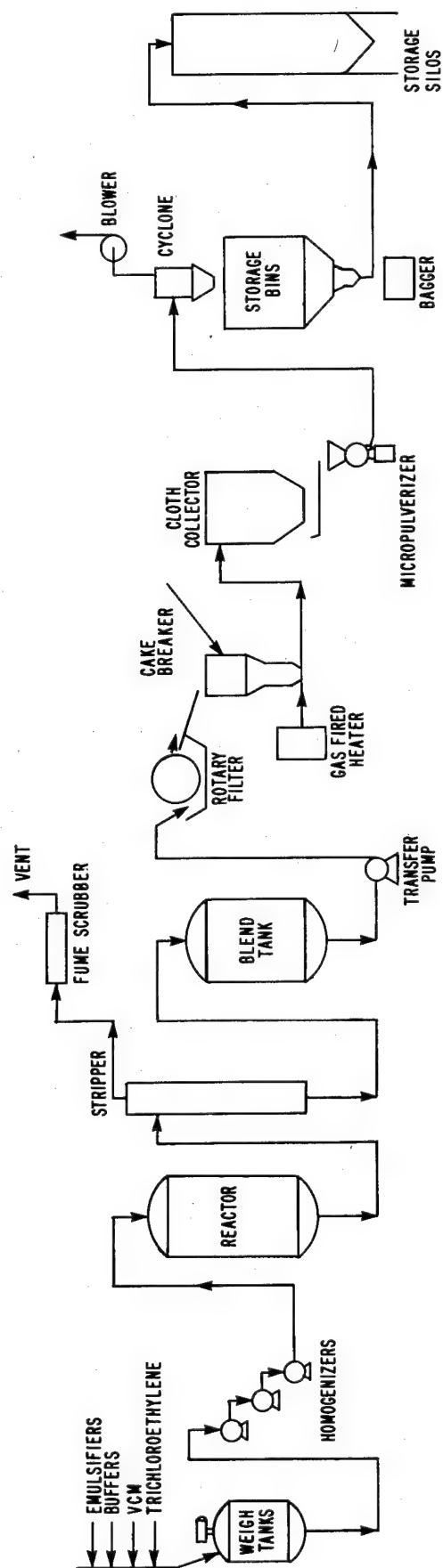


Figure A.4-1. PVC Dispersion Polymerization Process Flow Diagram

## Polyvinyl Chloride Dust

TWA 15 mg/m total dust

## Noise

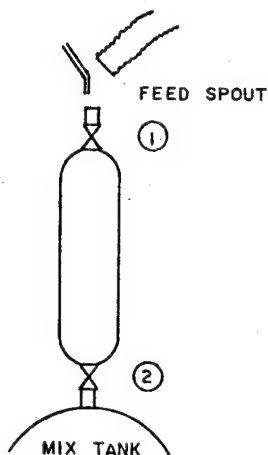
TWA 90 dBA

## CONTROL TECHNIQUES

### Process Design, Modification and Maintenance

#### Batch Mix Tanks--

As mentioned in the process summary, VCM is pumped into the batch mix tanks through a closed piping system. Hence, there is little chance of VCM escape during this operation. However, there is a potential for VCM escape when the minor batch ingredients are dumped into the mix tanks. This potential is reduced substantially by the use of a simple air lock entry system as depicted in the following diagram.



Valve 1 is opened and the ingredients are dumped through the feed spout into the air lock. Any dust or vapors generated are removed by the flexible exhaust duct positioned in the spout. Valve 1 is closed, valve 2 is opened and the ingredients drop into the tank. Valve 2 is then closed. Any VCM trapped in the air lock between batches would be exhausted when valve 1 is opened at the start of the next charging operation.

#### Homogenizer Pump System--

Because of periodic leaks from seals and discharges during maintenance on orifice sections, the homogenizer pump system has historically been a major source of VCM escape. Much improvement has been achieved by the installation of the local exhaust system described in a later section. However, this system could not contain VCM discharges during maintenance operations, since its primary function is the containment of small seal leaks. One major improvement involved connecting the homogenizer system to the stripper inlet piping. This allows liquid removal and VCM recovery of either an individual orifice section or the entire system prior to opening for maintenance operations.

#### Reactor Degassing Procedure--

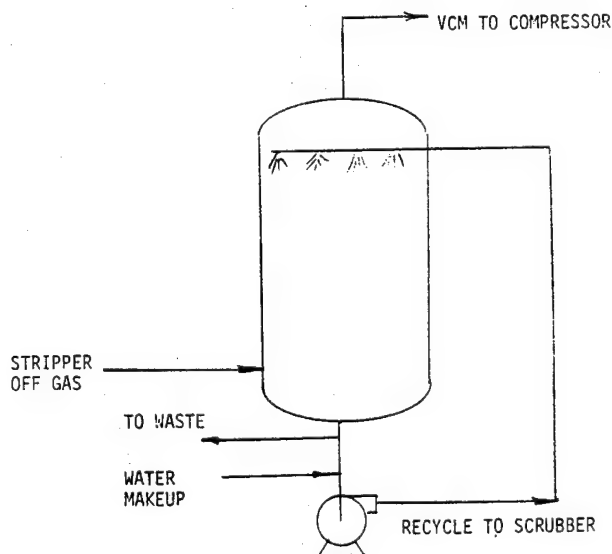
After the fully reacted PVC slurry is transferred from the reactor to the stripper, it is necessary to remove VCM from the reactor air space prior to opening the vessel for cleaning. The recovery compressor pulls suction on the reactor for about 1 hour to a vacuum pressure of 22 inches of mercury (previously 30 minutes and a vacuum pressure of 20 inches of mercury). Next, the reactor is purged with nitrogen, which is vented to the atmosphere. The exhaust system is hooked up at the bottom of the reactor and the manway is unbolted and lifted slightly to check the air flow. If there is no inward flow, the exhaust duct is checked for plugs and cleared and airflow is again checked. The manway is never opened fully until the airflow is assured. Next, the manway is removed and the reactor is purged with the ambient air. After approximately an hour, the high-pressure water lance is inserted into the top of the reactor and connected to a water hose inserted at the bottom of the reactor. (Prior to the use of the water lance, operators had to manually clean the reactor walls after each batch.) Finally, the cleaning water is drained from the reactor into an open trench sewer. Once a week the reactor bottom is cleaned with a 3D jet nozzle. This has eliminated another manual cleaning operation.

#### Stripping Process--

The stripping process takes place in an agitated vessel immediately downstream of the reactors. First, a vacuum is pulled by the recovery compressor. Then, nitrogen is introduced at the bottom of the vessel and is bubbled through the PVC slurry. The nitrogen is fed at a rate of 5 cubic feet per minute for about 7½ hours. No data were received on the VCM concentration in the slurry after the stripping operation. However, the slurry is still a source of VCM exposure downstream of the stripper, although the degree of hazard has been substantially reduced.

#### Fume Scrubber--

A fume scrubber consisting of an 8-foot diameter by 14-foot high cylindrical vessel with water spray nozzles is used to knock out any foam entrained in the gas leaving the stripper.



The major change in this system has been the use of heated make-up water in the scrubber. This has reduced VCM concentrations in the contaminated water coming from the stripper from a range of 100 ppm - 1000 ppm to a range of 5 ppm - 50 ppm. This reduces potential exposure around the drag out trench and lessens the potential of VCM re-entry into process areas. The scrubber also prevents foam carry-over into the blend tanks, which could cause pressure build-ups and a higher potential for leaks.

#### Slurry Blend Tanks--

In 1975, VCM excursions of 20 ppm to 150 ppm in the blend tank area were common. The first step in alleviating the problem was to seal and secure the tanks as much as possible. In addition, a local exhaust ventilation system (described in detail in a later section) was installed to exhaust the blend tank manways and agitator seals. Finally, the area was isolated outside of the building by relocation of the outside walls. Since employees rarely have to be in this area, the potential for exposure has been drastically reduced.

#### Vent and Exhaust Stack Relocation--

In 1975, a program was initiated to modify and relocate exhaust stacks and vents to prevent VCM from re-entering process buildings. This was a three-part process.

- (1) In the bagging and drying building, VCM excursions in the range of 10 ppm - 30 ppm were common. These excursions were traced to the primary and fine product collector exhausters. Each of these was extended and redirected.
- (2) The increased stripping and nitrogen purging in the reactors and strippers through the evacuation jets resulted in VCM concentrations up to 100 ppm at ground level. The stripper and reactor evacuation jets were relocated and extended.
- (3) The exhaust at the bottom of the reactor was discharged directly outside the building, resulting in high excursions throughout the plant area. All exhaust stacks were extended well above the reactor building roof.

#### Process Liquids Disposal--

Prior to 1975, VCM contaminated process liquids were drained to open sewers in the buildings. In most cases this procedure was modified to transport these liquids outside of the plant to open pits. However, this caused periodically high VCM excursions outside and frequently the VCM drifted into buildings and created employee exposure. Presently, most of the process liquids are piped to a closed holding tank for treatment and recycling or disposal. This change has affected a substantial decrease in the frequency and severity of VCM excursions.

#### WORK PRACTICES

Improved work practices have greatly facilitated the VCM control program. In large part, the improvement has been accomplished because of an increased awareness and concern by management, supervisors and maintenance and operations



personnel. The industrial engineer on the production manager's staff prepares monthly reports describing the nature of VCM excursions and the status of ongoing and/or future engineering control projects. Operating procedures are reviewed by the foremen and improved as necessary to reduce the potential for significant VCM escape.

One example concerning gasket usage is offered as an illustration of a good work practice. In 1975, the leak detection program identified a recurring problem with reactor manway gasket leakage which often led to VCM concentration in excess of 100 ppm. First, all new gaskets were examined and many were found to be defective. The problem was discussed with the vendor and subsequent shipments were satisfactory. Also, a significant portion of the leakage was determined to be a result of improper securing techniques by the reactor operators. A re-emphasis and retraining program was initiated and the frequency of leakage was subsequently diminished.

#### LEAK DETECTION AND PREVENTION

The leak detection and prevention program is divided into three parts:

- Leak Search and Secure: One employee tours the plant process areas with a portable hydrocarbon monitor, constantly checking for VCM leaks. The objective is to locate and contain minor leaks before they become extensive enough to contaminate wide areas and trigger the gas chromatograph monitoring network.
- Gas Chromatograph Monitoring System: Based on area sampling data, 21 process points were selected as optimum positions for employment of permanent air sampling heads. Samples are sequentially collected and analyzed on a 30-minute cycle. The detection system activates an alarm when any sample result exceeds a 5 ppm excursion limit. When the alarm sounds, employees are required to leave the work area or put on airline respirators.
- Excursion Analysis: Whenever the above monitoring system records an excursion over 5 ppm, a designated employee is required to determine the nature and location of the source with a portable hydrocarbon detector. The employee will attempt to correct the problem on site or contain the leak until proper maintenance can be performed.

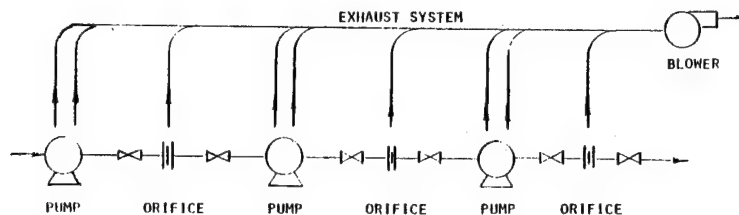
#### LOCAL EXHAUST VENTILATION SYSTEM

This system is somewhat different from those employed in other PVC processes because it is not designed for use on a "need" basis. Certain process points and vessels are provided with permanent exhaust takeoffs, which are not usually dampered or deadheaded when there is no leak. Eight individual systems, each with a separate blower, comprise the total system as follows:

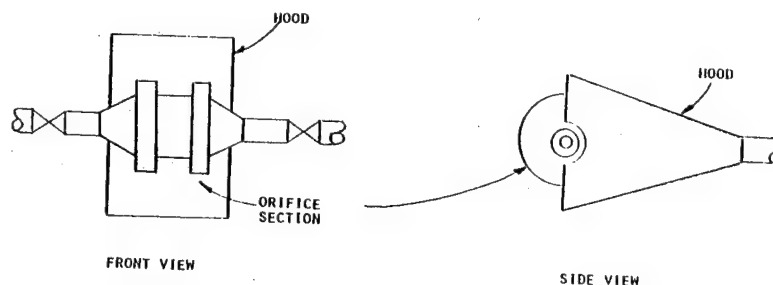
- (1) Batch Mix Tanks: The additive feed spout for each tank is equipped with a 6-inch flexible hose exhaust, which is permanently situated at the top, inside of the spout. Each flexible hose has a design airflow of approximately 0.52 m<sup>3</sup>/s (1100 cfm). Airflow measurements revealed a duct face velocity of 14.2 m/s (2800 fpm), or an airflow of approximately 0.26 m<sup>3</sup>/s (560 cfm). The reason for the inadequate airflow was

not determined. The effectiveness of the exhaust was judged to be good, although it would be preferable to permanently affix the duct to the side of the feed spout.

- (2) Homogenizer Pumps: The exhaust system for the homogenizer pumps is comprised of nine branches with a design airflow of  $0.85 \text{ m}^3/\text{s}$  (1800 cfm), or  $0.09 \text{ m}^3/\text{s}$  (200 cfm) per hood.

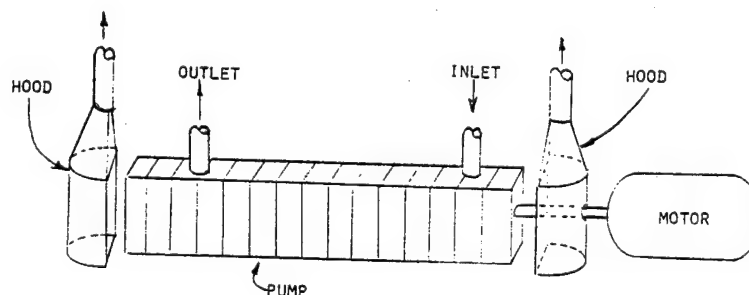


Orifice Sections: Each of the three orifice sections is provided with a hood as depicted in the diagram.



Measured hood face velocities in the hood averaged  $4.57 \text{ m/s}$  (900 fpm) in the center and  $2.54 \text{ m/s}$  (500 fpm) at the top and bottom. Based on a measured duct transport of  $15.2 \text{ m/s}$  (3000 fpm), the average hood airflow is estimated to be  $0.12 \text{ m}^3/\text{s}$  (260 cfm). This hood design is very effective in controlling small leaks from the orifice seals.

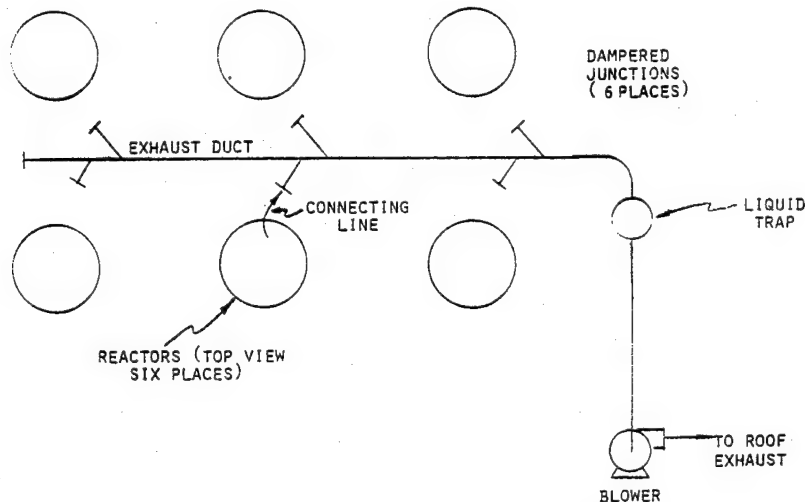
Pumps: The end of each of the three homogenizer pumps is equipped with a hood as depicted in the next diagram.



Duct transport velocities averaged  $15.24 \text{ m/s}$  (3000 fpm), or an estimated airflow per hood of less than  $0.05 \text{ m}^3/\text{s}$  (100 cfm). Hood face velocities were not measured because of the position of the ends of the homogenizer pumps. However, because the open area between the hood face and the pump ends is small, inward velocities should be well

over 0.51 m/s (100 fpm). Plant personnel indicated that these hoods are successful for containing small leaks but are not sufficient to contain VCM emissions resulting from major seal failures.

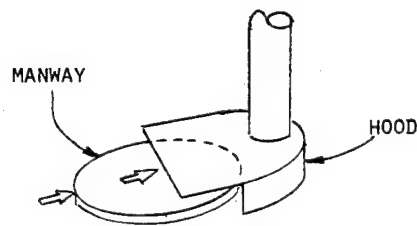
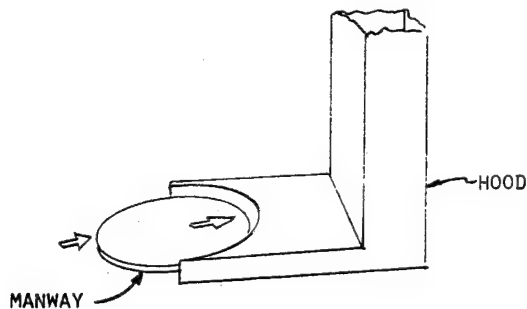
- (3) **Reactor Exhaust:** This system is based on the fact that only one reactor will be open for cleaning at any one time. A flexible duct connector is inserted into the appropriate branch junction (the other five junctions are dampered) and a coupling at the bottom of the reactor is opened and airflow is initiated. One problem with the system is that it is used initially to remove residual slurry from the vessel. Although there is a liquid trap (sealed metal barrel), pluggage is common, particularly in the connector hose. The airflow through the system was estimated as 0.06 m<sup>3</sup>/s (130 cfm), based on the 4-inch duct transfer velocity of 7.62 m/s (1500 fpm). The blower capacity is not known but it is judged to be considerably higher than 0.06 m<sup>3</sup>/s (130 cfm). Probably, liquid has accumulated in the blower and caused a reduction of the rated airflow.



However, the system induced an inward airflow of about 0.51 m/s (100 fpm) through the open manway at the top of the reactor. Calculations reveal that the airflow rate of 0.06 m<sup>3</sup>/s (130 cfm) will produce slightly over eight reactor air changes during the exhaust period of 1 hour.

- (4) **Blend Tanks:** Each of the three blend tanks is equipped with an exhausted hood for the manway. In addition, since the agitator shafts are not sealed, they are shrouded and exhausted. The ventilation system is supplied with a blower of 1.04 m<sup>3</sup>/s (2200 cfm) capacity, or an average of about 0.19 m<sup>3</sup>/s (400 cfm) per hood or shroud.

**Manway Exhaust Hoods:** Measured capture velocities for all types of hoods ranged from about 1.78 m/s to 2.03 m/s (350 fpm/400 fpm) at the center point of the manway, to 100 fpm at the opposite end from the hood. This airflow should be quite sufficient to contain VCM leaks from the manway.



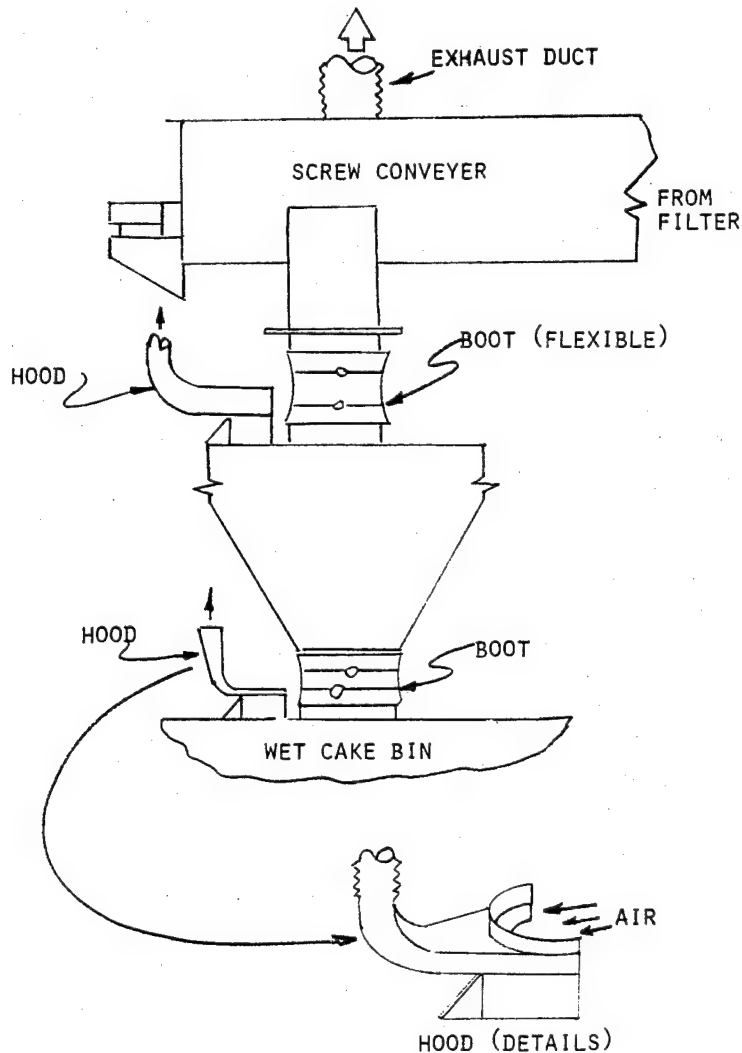
Agitator Shaft Shroud: A flexible exhaust duct has been inserted into the shroud surrounding the agitator shaft. Air velocities through open spaces in the shroud opposite the exhaust duct were measured at 2.03 m/s (400 fpm).

- (5) Filter Enclosure: Each rotary cloth filter was totally enclosed with a sheet metal structure. Removable side panels were installed to allow maintenance operations and filter cloth changes with minimum disruption to the exhaust system. Each enclosure is exhausted at a rate of 3.87 m<sup>3</sup>/s (8200 cfm), or a calculated rate of over 100 air changes per hour. The enclosure panels on one side of the filter were removed and average inward velocities ranged from 0.71 m/s to 1.02 m/s (140 fpm/200 fpm). Plant operating and engineering personnel are convinced that these exhausted filter enclosures have been the most effective VCM control method implemented to date.
- (6) Cake Breaker and Wet Cake Bin: The screw conveyor, which empties the wet PVC cake into the cake breaker, is under negative pressure because of the flexible exhaust duct depicted below. This prevents VCM from escaping to the workplace if there are leaks or open spaces in the conveyor.

There have been problems with plugging in the rubber dump connections or boots between the conveyor and the cake breaker, and the cake breaker and the wet cake bin. The rubber boot frequently has to be removed to clear the obstructions. During these operations the hoods depicted in the following diagram are used to control VCM release. Average face velocities were measured at 3.30 m/s (650 fpm) to 9.14 m/s (1800 fpm).

When the boots are in place, the hoods help to contain VCM leaks from the boot connection. The system is judged to be relatively effective in controlling small leaks, but probably does not provide adequate

containment when the boots are removed for maintenance. However, the improvement is marked over the time before the exhaust hoods were installed.



- (7) VCM Feed Pumps and Recovery Compressors: Many pump and compressor seals are shrouded and locally exhausted. Thus, when there is a leak in the seal, workplace contamination with VCM is prevented or greatly reduced.
- (8) Auxiliary Local Exhaust: As an adjunct to the above exhaust systems, there are numerous small mobile blowers,  $0.19 \text{ m}^3/\text{s}$  (400 cfm) each, which are used to contain leaks as needed. A flexible duct is positioned at the leak source, and another flexible hose from the blower outlet is placed next to a wall-mounted exhaust fan. Although it would be preferable to exhaust these blowers to the vent stacks, most of the VCM contaminated air is removed from the workplace and normally does not re-enter.

## GENERAL EXHAUST VENTILATION SYSTEM

The process building exhaust fans have been in place for some time, so design specifications were not available. The fans were located such that airflow could not be measured. Hence, no data are presented on existing air turnover due to this system. It was surmised that there is adequate dilution ventilation to effect a relatively rapid dissipation of VCM concentrations following a leak.

There are many wall-mounted fans which are activated in emergency situations when VCM concentrations may approach 50% of the lower explosive limit. Since VCM is much heavier than air, the fans are located close to the floor. The wall-mounted fans are normally on during the summer.

In May 1975, an employee monitoring program was initiated. Charcoal tubes were used to obtain 8-hour personal samples on a monthly basis. Average TWA exposures are compared below (Figure A.4-2) for the appropriate job functions during 1975 and 1976.

It is clear from this plot that employee exposure has been significantly reduced since the engineering controls were implemented. Two comments are necessary:

- The plot shows that the dispersion area foreman received an increase in exposure in 1976 relative to 1975. This is largely due to one extremely high sample result causing an average 1976 TWA exposure of 9.3 ppm. If this one reading is not included, the exposure average for 1976 drops to 0.8 ppm.
- Although a substantial reduction in reactor cleaner exposure has been achieved, the average exposure for 1976 is still excessive. It is noted that air line respirators are worn during reactor cleaning since high VCM excursions are sometimes encountered.

In April 1975, the process gas chromatograph monitoring system was installed. Since that time, an extensive amount of data has been developed for each of the 15 sampling points. These data (shown in Figures A.4-2 and A.4-3) illustrate the beneficial effect of the engineering controls. It should be pointed out that these data are area samples and do not directly reflect employee exposure. Further, many sampling heads are located in the same general process area, and an emission at one point influences the reading at several others. Thus, it is difficult to draw conclusions concerning individual control effectiveness from sampling point data.

The reduction in average VCM concentrations between 1975 and 1976 is very apparent. All except three sample points average below 1 ppm. (The VCM charge pumps and the blend tanks are in areas that are not work stations, and employee exposure times are minimal. The reactor penthouse is an area where supplied air respirators are required for entry.)

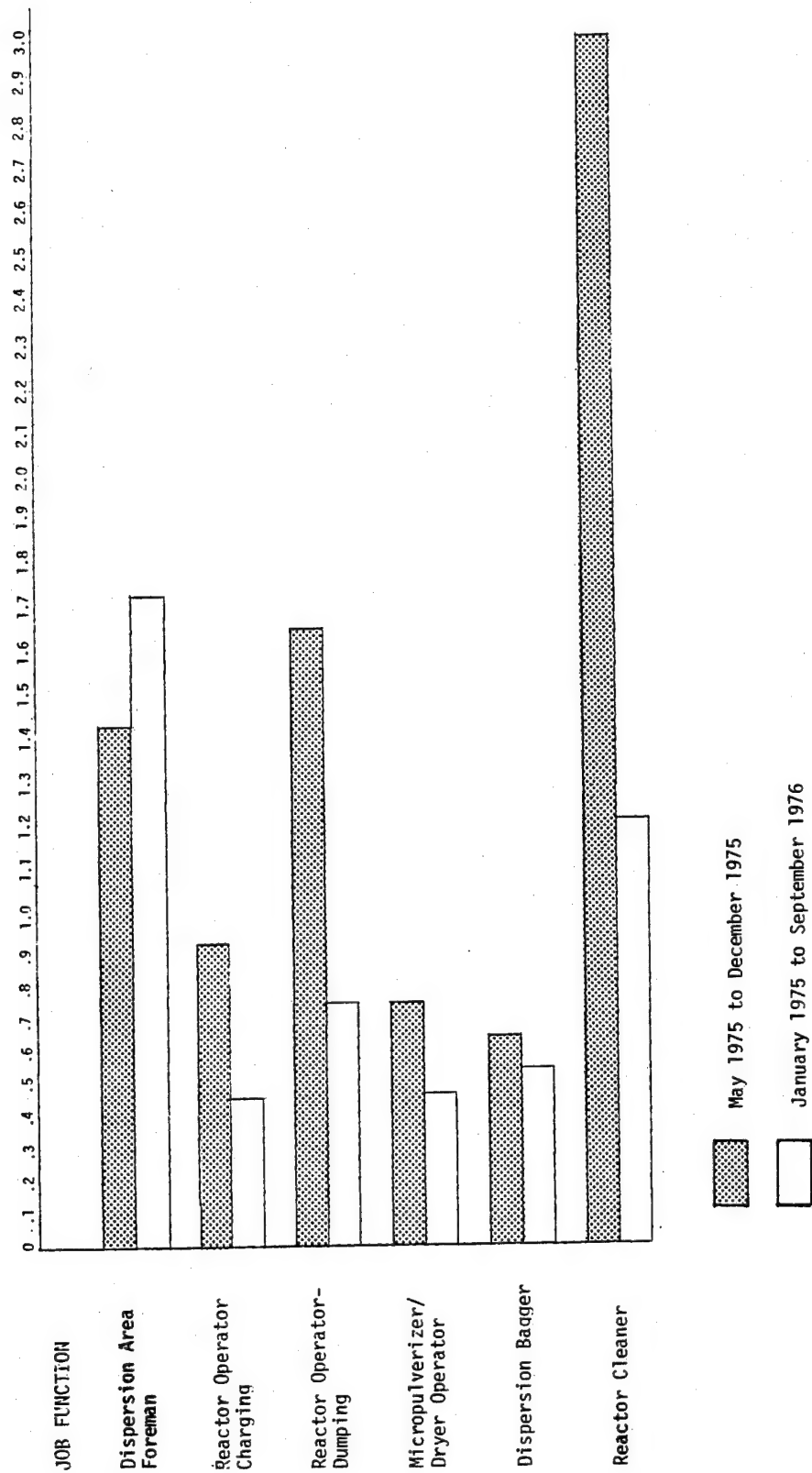


Figure A.4-2. Employee Exposure by Job Function

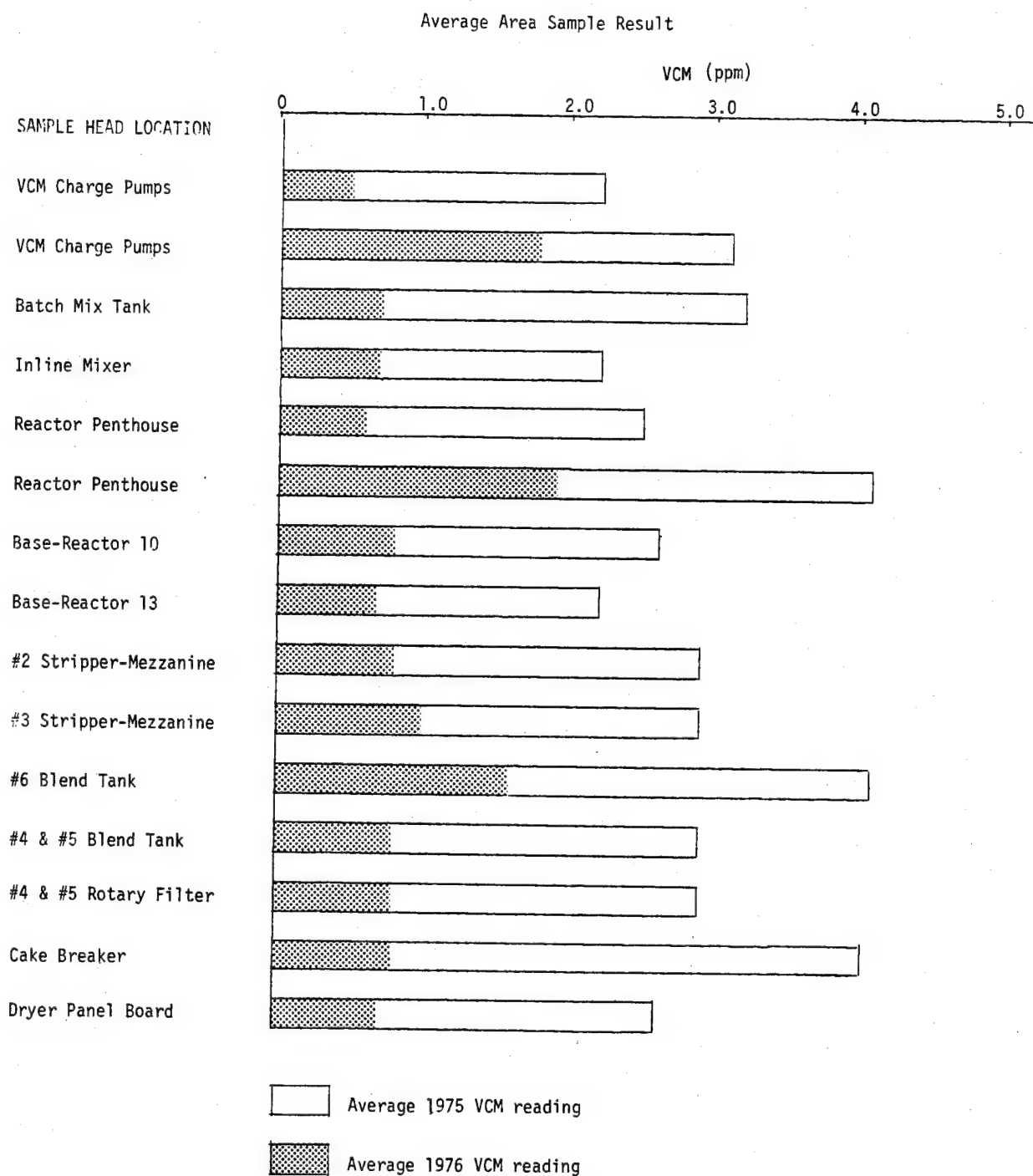


Figure A.4-3. Average Area VCM Concentration at Work Stations



## PERSONAL PROTECTIVE EQUIPMENT

Supplied air line respirators are required for operators in process areas when the gas chromatograph monitoring system alarm indicates a VCM concentration in excess of 5 ppm. Supplied air line respirators must always be worn by employees entering the reactor penthouse. They must also be worn during certain maintenance operations which have been determined to be significant sources of VCM escape.

## CONTROL TECHNIQUES FOR OTHER POTENTIAL HAZARDS

### PVC Dust

PVC dust is generated in the micropulverizer room and at the dispersion resin baggers. Gravimetric personal samples revealed the following average time-weighted exposures:

Dispersion Resin Bagger	0.13 mg/m <sup>3</sup> total dust
Micropulverizer Operator	2.80 mg/m <sup>3</sup> total dust

Both of these exposure levels are well below the limit for nuisance dust of 15 mg/m<sup>3</sup> total dust.

No dust containment controls were noted in the micropulverizer room. The operator spends much of his time at a control panel in the utility building; hence, exposure time is limited.

The dispersion resin holding hopper is under a negative pressure, and this reduces the potential for dust escape. No specific dust control measures were noted in the bagging area.

### Noise

Most noise abatement measures have been directed at environmental sources such as blower intakes and outlets for the air conveyance and local exhaust systems. Controls have included the installation of commercially available silencers on the intakes and mufflers on the exhausts. Although these sources are outside the work area, their attenuation does assist in reducing worker exposure.

<u>Location</u>	<u>Sound Levels (dBA)</u>	<u>Source-Comments</u>
Micropulverizer Room		The vibrators and pumps are the primary sources, although vibrations radiating through the ductwork contribute significantly to the high noise levels. Workers who enter the area must wear a combination of ear plugs and muffs. Even with this hearing protection, employees are prohibited from spending more than 3
Overall	105	
Near Vibrators	115	

<u>Location</u>	<u>Sound Levels (dBA)</u>	<u>Source-Comments</u>
		hours per shift in this area. Doors are kept shut to localize the noise exposure as much as possible.
Bagging Area Outside of Micropulverizer Room	95-97	Sources include the bagger, vibrations radiating through pipes, and noise from the shakers and vibrators located directly above. Noise levels may be reduced by acoustically isolating the area from the overhead area, lagging the conveyor pipes, silencing air discharges and improving equipment maintenance.
Process Building Batch Mix Tank	85-86	Hearing protection not required.
Operator Panel	83-84	Hearing protection not required.
Dumper Operation Station Between Two Strippers	87	Hearing protection not required.
Homogenizer Pumps Running	93	Homogenizer pumps are operated for an average of 1½ hours per shift. Hearing protection is not required.
Not Running	87	

## APPENDIX A.5. PVC DISPERSION AND SUSPENSION PROCEDURES - CASE STUDY NO. 5

### INTRODUCTION

This case study involves both a suspension and dispersion process. These are not presented separately because they are in the same building and, thus, have common computer control, VCM recovery, monitoring and general ventilation systems, as well as common process equipment and operators. In fact, most of the control techniques are identical. Therefore, after each process is summarized, a combination of separate and common controls are to be described.

### SUSPENSION POLYMERIZATION PROCESS SUMMARY

Figure A.5-1 presents a simplified flow diagram for the suspension polymerization process. Very small quantities of catalyst and other additives are added to an empty reactor through an open manway. The manway is then closed and the reactor evacuated to remove the air. The suspension solution, water and vinyl chloride are pumped into the vessel through a metering system. Any vinyl chloride remaining in the feed line is flushed into the reactor with water.

The reaction is initiated by heating the charge with a steam sparge. Once the reaction begins, the external heat is stopped. The internal heat of reaction is removed and the temperature is controlled with immersed cooling baffles and water jackets.

At the completion of the reaction cycle, the gas phase in the reactor is vented to a blow down tank to disengage any resin carry-over. The slurry is then pumped to a holding tank and residual vinyl chloride is removed from the reactor and recovered.

The slurry is pumped from the holding tank through stripping column using steam as the stripping medium. The stripped slurry is pumped to blend tanks and various batches are mixed to provide uniformity. From the blend tanks, the slurry is pumped to a centrifuge where the PVC particles are separated from the process water. The wet PVC cake is dropped into a flash dryer, and any remaining moisture is driven off. A pneumatic system transfers the dry PVC particles to holding hoppers, through which they are gravity fed into a series of vibrating screens. Oversize PVC is packaged and sold as off-grade product. The PVC passing through the screens is transferred to storage silos for bulk shipping, bagging or compounding operations.

### DISPERSION POLYMERIZATION PROCESS SUMMARY

A flow diagram illustrating the essential elements of the dispersion polymerization process is presented in Figure A.5-2.

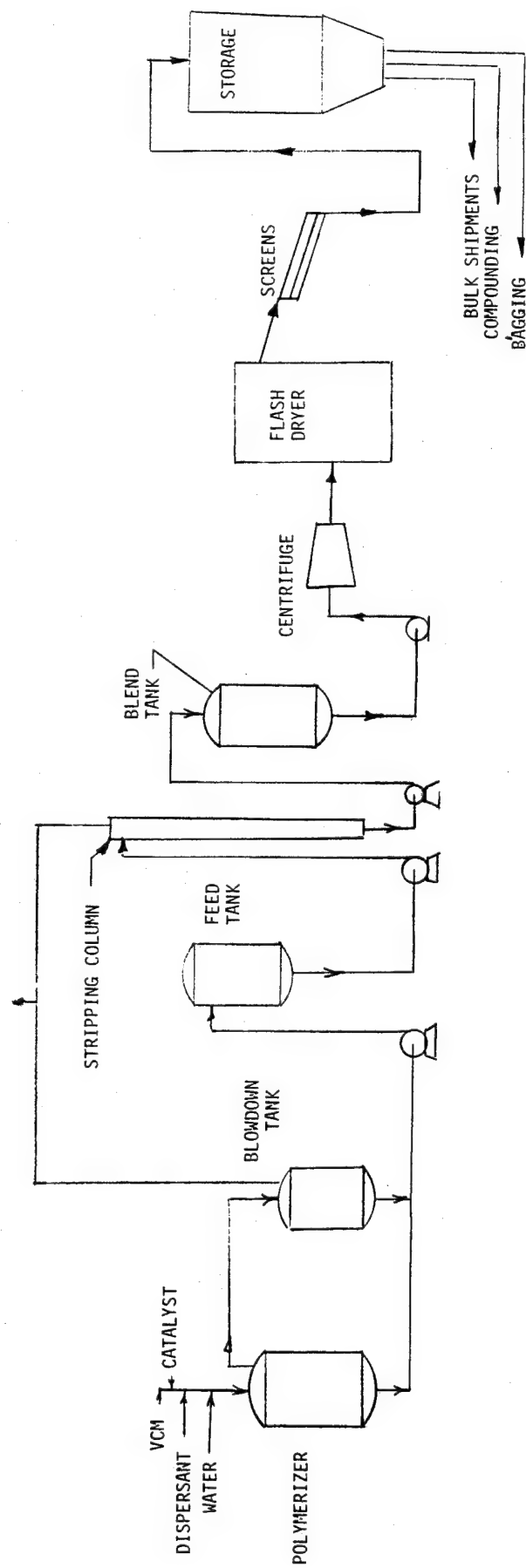


Figure A.5-1. PVC Suspension Process Flow Sheet

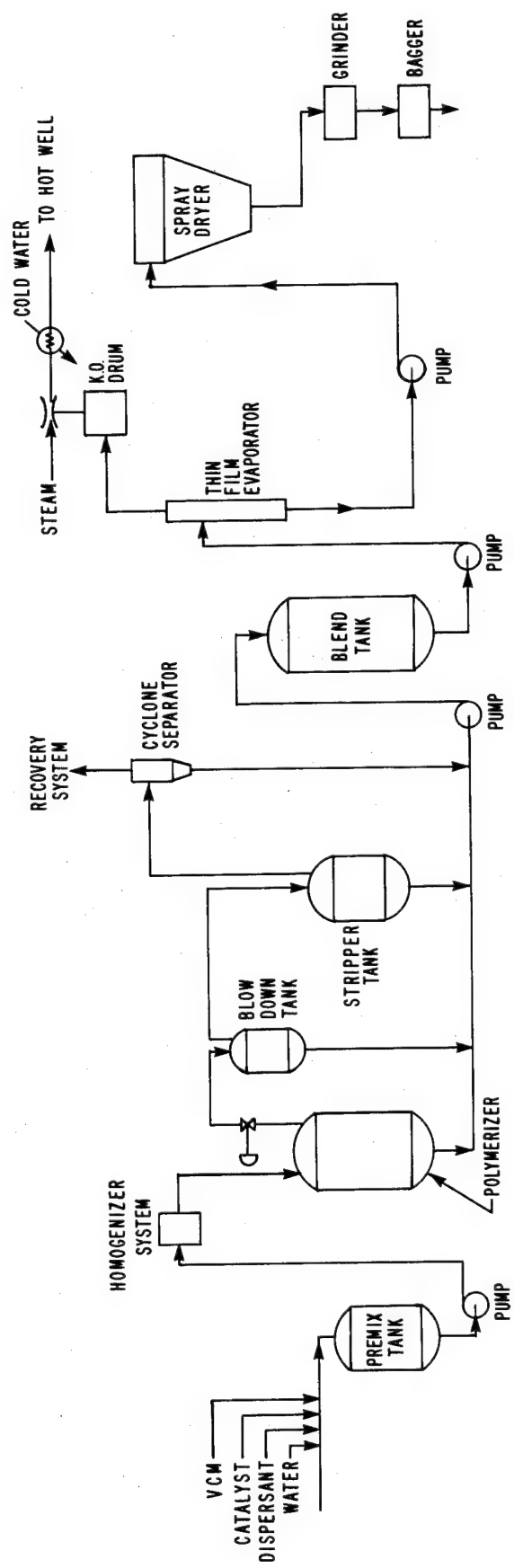


Figure A.5-2. PVC Dispersion Process

The initial charge to the premix chamber consists of weighed quantities of water and dispersants. The catalyst is added to a holding chamber and vinyl chloride is used to wash it into the premix chamber. Additional vinyl chloride is metered in as needed to meet required batch weight specifications. The final rinse through the catalyst holding chamber is with water to eliminate an exposure source when the chamber is opened for the next batch.

The two-phase suspension is dispersed and pumped to the bottom of a reactor. When the reaction cycle is completed, the vapor phase is transferred from the top sequentially through a blow down tank, a stripper tank and finally a cyclone separator. The cyclone separator disengages the liquid and solid phases from the vinyl chloride.

The liquid phases from the reactor; the blow-down tank, the stripper tank and the cyclone separator are pumped to an agitated blend tank. The blended emulsion is pumped to a concentrator consisting of a thin film evaporator. The concentrated emulsion from the evaporator is pumped to a spray dryer.

The spray dryer removes the liquid phase from the emulsion and the tiny PVC particles fall into a pneumatic conveyor. The PVC particles are collected, ground, screened and then packaged.

#### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

Although some of the minor batch ingredients may be different, both processes present essentially the same exposure to the operators.

##### Vinyl Chloride

TWA 1 ppm, ceiling limit 5 ppm for any 15-minute period

##### Polyvinyl Chloride Dust

TWA 15 mg/m<sup>3</sup> total dust

##### Noise

TWA 90 dBA

#### CONTROL TECHNIQUES

##### Computer Control of Process

With a very few exceptions, each process is computer-controlled. This allows a reduction in employee exposure because 1) the number of operators required to run the process is decreased; 2) the operators spend a significant amount of time in an enclosed control room (where exposure is essentially zero) maintained at a pressure slightly higher than the outside; and, 3) operators do not have extensive interaction with the process which eliminates errors and the concomitant exposures. Thus, the number of exposed employees, the amount of time spent in a potentially hazardous area and the likelihood of significant releases of vinyl chloride are all reduced.

## Suspension Process Stripping Column

The most effective control technique to date is the development of a stripping column that removes residual vinyl chloride from the PVC slurry following the reaction. Plant personnel have data to demonstrate that employee exposure to vinyl chloride has been eliminated at all operations downstream of the stripping process.

## Suspension Reactor Cleaning Procedures

The major source of exposure upstream of the stripping column is opening the reactors for cleaning after each cycle. Modifications that have been implemented to assist in controlling VCM escape are:

### Degassing Process--

Since the reactors are opened after each cycle, it is beneficial to first reduce vinyl chloride concentrations in the vapor space to a minimum. When the reaction has been completed, the pressure in the reactor (~100 psi) is used to vent the VCM and water vapor through a blow-down tank to the recovery system. The rate at which the vapors leave the blow-down tank is controlled to stay within the operating requirements of the recovery heat exchanger (refrigerated water at 7°C [45°F]). When the pressure in the reactor drops to 40 psi, the PVC slurry is pumped to a holding tank prior to transfer to the stripping column. A compressor is used to pull vacuum on the reactor and the blow-down tank. At the proper time, each vessel is steam sparged and vinyl chloride concentrations are further reduced. Finally, air is introduced into the vessels to equalize the pressure and the manway is opened without significant releases of VCM.

### Reactor Cleaning--

At one time, operators were required to enter and manually clean the reactors after each batch. The frequency of entry was reduced to every 25 to 30 batches by the use of a high pressure (4000-6000 psi) HRC water jet cleaning system. The water jet collar fits directly into the reactor manway, and has been modified to incorporate a four-inch flexible duct so that the reactor can be exhausted while being cleaned. Contaminated cleaning water is pumped to a sump located outside the building.

The entry and cleaning frequency has been further reduced to once every 100 batches by the development of a proprietary anti-buildup coating.

## Dispersion Reactor Cleaning Procedures

A stripping process for the dispersion resin is planned, but has not been installed as yet. However, to reduce vinyl chloride escape to the workplace when the reactors are opened for cleaning (after every batch), a degassing sequence is employed. When the reaction has proceeded to completion, a vacuum is pulled on the reactor to remove unreacted vinyl chloride from both the resin and the reactor vapor space. Steam is injected into the water jacket to accelerate and optimize the effectiveness of the degassing process.

However, this procedure is slow and there are plans to install a two-phase degassing system. The details of this system are now available.

The reactor cleaning procedure for the dispersion resins is identical to that described for suspension resins; i.e., a high pressure HRC water jet system is used. Through the use of a water jet system, the entry frequency has been reduced to once every 5 to 15 batches. In addition, work is under-way to develop a formulation which results in less buildup on reactor walls.

### Suspension Strainers

The PVC slurry from the reactors originally passed through a strainer basket which removed oversize PVC particles. The basket frequently had to be disassembled for cleaning, resulting in large releases of VCM. The strainer basket has since been replaced with an in-line comminuter which grinds up any large particles passing through it and, thus, seldom has to be opened for cleaning or maintenance.

### High Pressure Recovered VCM Filter

Another significant source of employee exposure for both processes was the frequent maintenance operations necessary to clean the high pressure recovered VCM filter.

When the filter was neglected until totally plugged, extensive time was required for maintenance and exposure to VCM was very high. This problem has been reduced by cleaning the filters on a routine basis; that is, before they become totally plugged. A hot water (71°C [160°F]) injection system was installed to reduce the amount of vinyl chloride in the filter prior to opening. This has appreciably reduced the exposure potential associated with changing the filters.

### Process Water Disposal

Previously, process water contaminated with vinyl chloride was dumped from the reactors into an open sewer system inside of the building. When this was done, VCM concentrations throughout the building were significant. Currently, all process water is pumped to an outside sump, where residual vinyl chloride is atmospherically dispersed without contributing to employee exposure.

## LEAK DETECTION AND PREVENTION

Rapid leak detection is critical to the success of the vinyl chloride control program for both processes: 1) It allows the timely containment and/or repair of leaks soon after they occur (since most leaks develop slowly, they may be contained before large emissions of vinyl chloride develop) and, 2) It assists in reducing exposure by activating visual alarms when hazardous concentrations of vinyl chloride exist and respiratory protection is necessary.

The basis of the system is a process chromatograph monitoring network consisting of a number of strategically placed air sampling heads. Air samples are collected and analyzed sequentially from each process point over a cycle of less than 10 minutes. The system is tied into the computer so that any level from 1-5 ppm will set off alarm lights, requiring that respirators be used or that employees evacuate the area to the control room.

Once a warning light is activated, an employee will use a portable hydrocarbon



detector to determine the exact location of the leaks, or the local exhaust system is used to contain the leak and a maintenance work order is made out. The nature and location of each leak is recorded and these records are periodically analyzed for trends and planned engineering needs.

### Important Equipment Features

The double mechanical seals that are successfully being used with compressors, pumps and agitators are listed in Table A.5-1. These seals are common to both the dispersion and suspension processes. Seals that are used with process streams containing VCM are pressurized with a solution of glycerine and water. The glycerine is compatible with the process stream and reduces the risk of freezing of the seals in cold weather.

TABLE A.5-1. Seals for Compressors, Pumps and Agitators

Application and Vendor	Seal Manufacturer	Seal Model No.
VCM Recovery NASH Vacuum Pump Model CL702	Crane	Type 8B2
VCM Recovery NASH Compressor Model H6	Crane	BBL Type 8-1 Pressurized with water
Pumping Liquids Containing VCM Durco Pump	Crane	Type 9T
Agitator Shaft Seal	Crane	Type 9, 90 and 80 dual mechan- ical seals
	Pfautler	Oil pressure unit for pres- surizing dual mechanial seal
Tank Farm Unloading Lines Quick Disconnect Coupling Andrews Co. Model 400D		

## LOCAL EXHAUST VENTILATION SYSTEM

### Suspension Polymerization Process

The primary objective of this system is to minimize vinyl chloride escape from the reactors when they are opened for cleaning and when operators have to enter for manual cleaning. Each reactor is equipped with two flexible exhaust hoses suspended from the main duct through rigid sleeves. One of the flexible exhaust hoses is inserted into the reactor manway immediately after it is opened. When the high pressure jet water cleaning system is placed in the manway, the flexible hose fits into a four-inch sleeve in the HRC frame. Thus, the reactor is continually exhausted throughout the time it is open. When the reactor is closed, the flexible hose is dampered or used to remove vinyl chloride from any leaks in the area of the reactor.

The other flexible exhaust hose fits into an enclosure over the vacuum break valve. This hose provides additional exhaust to the reactors when they are open for cleaning. Since the break valve is open only when the manway is open, the exhaust is dampered when the reactor is closed.

Also included in the system are two 25-foot flexible exhaust hoses used as all-purpose maintenance drops, an exhaust takeoff for the high pressure recovered vinyl chloride filter and an exhaust takeoff for each of the two PVC slurry strainers.

The design airflows for each of the exhaust branches are:

● Reactor vacuum break valve	0.09 m <sup>3</sup> /s (200 cfm)
● Reactor evacuation hose	0.30 m <sup>3</sup> /s (625 cfm)
● Slurry strainers	0.14 m <sup>3</sup> /s (300 cfm)
● High pressure recovered vinyl chloride filter	0.28 m <sup>3</sup> /s (600 cfm)

The pressure drops are not specified as to design airflow as they are only opened during a maintenance operation. The system airflow capacity was designed so that no more than three of the eight reactors can be opened at any one time. The exhaust takeoffs for the slurry delumpers and high pressure filter were designed to operate continuously. Relative to this design parameter, actual airflows will be at least equal to the above design specifications.

Airflow measurements were taken in an open reactor manway with both exhausts in place and operating. The average inward velocity in the manway was 1.27 m/s (250 fpm). This is quite sufficient to prevent VCM escape into the workplace.

The one weak point in the system is the potential of vinyl chloride escape between the time the reactor manway is opened and the evacuation hose is inserted. Plant engineers have experimented with a valve system that would enable the evacuation hose to be inserted into the reactor before the manway is opened. However, the negative pressure that this induced on the reactor was sufficient to cause major problems in opening the manway. Pressure-equalizing intake valves were considered and discounted because of the

increase in the potential for vinyl chloride escape through the two additional valves when the manway is closed and the reaction in the reactor is underway.

Two adjuncts to the existing local exhaust system have been developed to be used as needed. The first item assists in controlling leaks through the reactor manway gaskets. Such leaks are relatively prevalent because of nicks and scratches on the sealing surface of the manway hatches. This is further complicated if resin particles are permitted to accumulate between the hatch and its seat during cleaning operations. It was determined through experience that these leaks could not be contained adequately solely by placing the reactor evacuation duct in the approximate position of the emission. This problem was solved by fabricating flexible rubber hoods which can be placed over the entire manway, if a leak occurs. The evacuation duct may then be inserted into a sleeve in the hood and any leaks are effectively controlled until the manway is opened. As a permanent solution, all manways are being rebuilt to restore a smooth sealing surface. Cleaning procedures have emphasized the importance of preventing any resin accumulation on the gasket or the sealing surface.

The second local exhaust aid is simply a metal drum fabricated with an exhaust duct sleeve at the top end. The drum covers the funnel that drains the compressor-cooling water from the compressor system. If contaminated seal water leaks into the cooling water, the maintenance drop exhaust duct is inserted into the drum and the potential for vinyl chloride escape into the workplace is eliminated.

#### Dispersion Polymerization Process

The local exhaust ventilation system for the dispersion polymerization process consists of three sections, each with its own blower.

The first provides control for periodic operations, primarily opening the reactors for cleaning following each batch. The system is divided as follows:

- Reactor Evacuation Ducts -  $0.30 \text{ m}^3/\text{s}$  (625 cfm) each. A 20-foot flexible hose is inserted into the open manway when the reactor is opened. When the reactor is closed, the ducts are either dampered or used to contain small VCM leaks in the area.
- Reactor Vacuum Break Valve Ducts -  $0.09 \text{ m}^3/\text{s}$  (200 cfm) each. A 4-foot flexible hose is inserted into the enclosure around the vacuum break valve. When the reactor is cleaned, the valve is opened and the line provides suction on the reactor. When the reactor is not being cleaned, the valve is closed and thus the duct is deadheaded. (There has been a problem with water accumulation in the duct elbow which clogs the exhaust. This could be alleviated by installation of a drainable liquid trap in the line.)
- Two All-Purpose Maintenance Drops -  $0.09 \text{ m}^3/\text{s}$  (200 cfm) each. A 25-foot flexible hose is used as necessary to contain any VCM leaks located in the area. These ducts are deadheaded when not needed.
- One Catalyst Bottle Exhaust Hood -  $0.36 \text{ m}^3/\text{s}$  (760 cfm). A simple canopy hood is positioned over catalyst bottle and dampered unless a reactor is being charged.

The airflow values listed above are based on an assumption that no more than seven branch ducts are open at any one time. This is a good design as long as no more than three reactors are opened for cleaning at one time (certainly a very rare occasion).

The second section provides continual exhaust for process points determined to have a relatively high leak potential. They consist simply of an enclosure and four-inch exhaust sleeve around the potential leak source, with a flexible exhaust duct fitted into the sleeve.

- Resin strainers  $0.14 \text{ m}^3/\text{s}$  (300 cfm)
- Product filter  $0.14 \text{ m}^3/\text{s}$  (290 cfm)
- Two homogenizers  $0.12 \text{ m}^3/\text{s}$  (210 cfm)
- Premix pumps  $0.10 \text{ m}^3/\text{s}$  (210 cfm)
- Seal water filter  $0.14 \text{ m}^3/\text{s}$  (300 cfm)
- Recovered VCM filter  $0.09 \text{ m}^3/\text{s}$  (200 cfm)
- VCM charge pump  $0.09 \text{ m}^3/\text{s}$  (200 cfm)
- Can pump (outside)  $0.09 \text{ m}^3/\text{s}$  (200 cfm)

The location of these permanent exhaust takeoffs were carefully considered and selected on the basis of area monitoring analyses.

The third section provides a negative pressure on each of two emulsion blend tanks at a low rate of  $0.71 \text{ m}^3/\text{s}$  (1500 cfm) each.

#### GENERAL EXHAUST VENTILATION SYSTEM

The general exhaust ventilation system depicted in Figure A.5-3 is for both the suspension and the dispersion processes. The building has two floors so there are essentially two systems.

The second floor contains the tops of the reactors, the premix tank, the homogenizers, the top of the blow down tanks, the low pressure filter, the metering station and the recovery pump and compressor. During the summer, the exhaust provides approximately 27 air changes per hour ( $31.81 \text{ m}^3/\text{s}$  [67,400 cfm] of exhaust and  $15.91 \text{ m}^3/\text{s}$  [33,700 cfm] of forced makeup air). The floor is thus under negative pressure and additional air enters through the louvers and any other open spaces. In emergency conditions, the ventilation rates are identical to those during summer, except that the three roof fans are not operated.

In winter, the system provides about 13 air changes per hour ( $15.86 \text{ m}^3/\text{s}$  [33,600 cfm] of exhaust and an equal volume of tempered makeup air).

The first floor contains the bottoms of the reactors and blow-down tanks, the stripping tanks, the compressor seal tanks, a water tank and the recovered vinyl chloride charge pumps and filters. During summer, the exhaust provides 25 air changes per hour,  $30.96 \text{ m}^3/\text{s}$  (65,600 cfm) of exhaust and  $17.37 \text{ m}^3/\text{s}$  (36,800 cfm) of forced makeup air. The remaining makeup air enters through the louvers and any other openings to the outside. In emergency conditions, exhaust rates are identical to those provided in the summer. In winter, there are 13 air changes per hour,  $15.48 \text{ m}^3/\text{s}$  (32,800 cfm) of exhaust and  $17.37 \text{ m}^3/\text{s}$  (36,800 cfm) of tempered makeup air. The louvers are closed during winter.

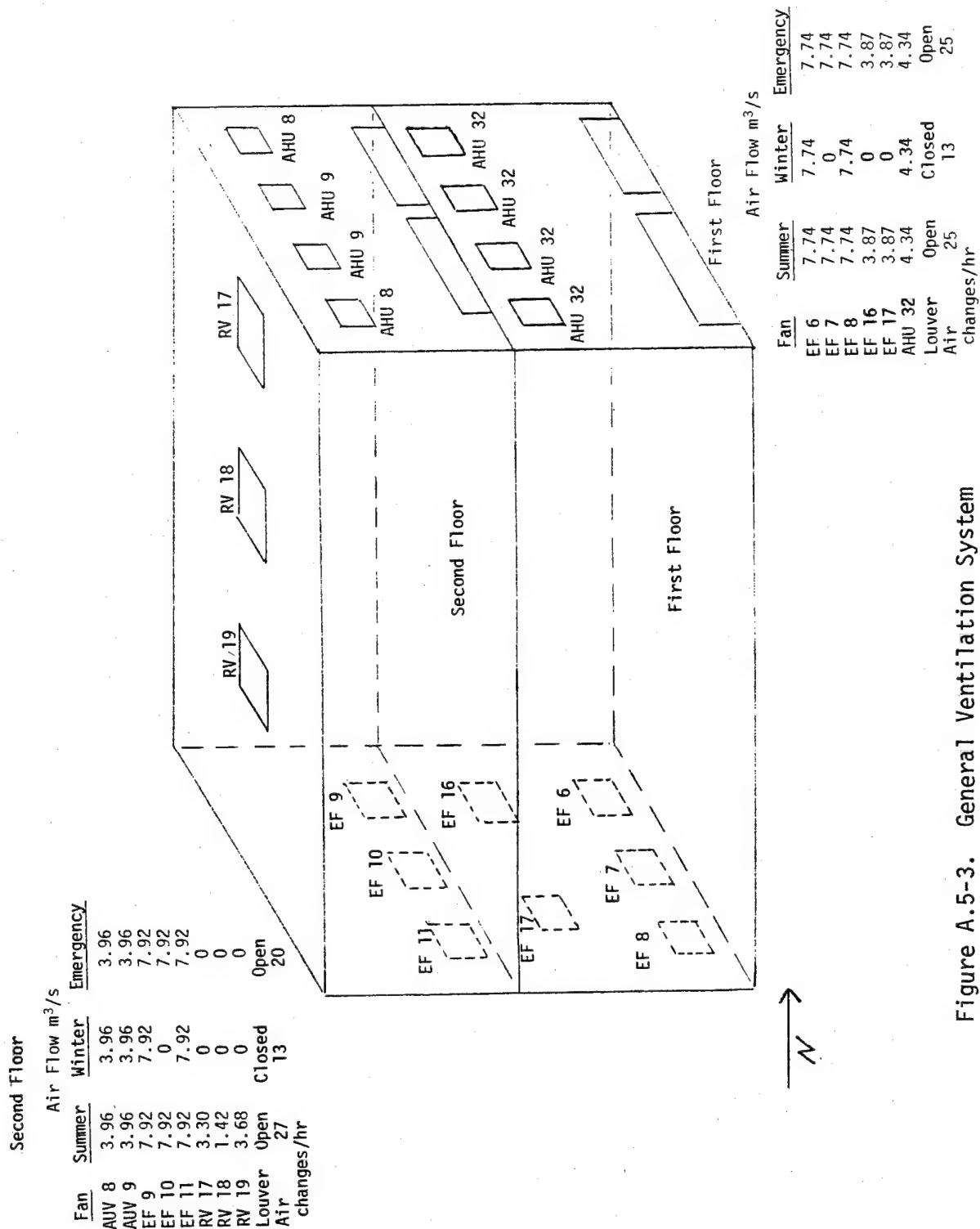


Figure A.5-3. General Ventilation System

The system is designed to produce a relatively consistent airflow pattern from the north end to the south end of the building. In terms of the two processes, the airflow moves from the suspension process past the dispersion process. This reduces the possibility of air stagnation areas or dead air pockets where vinyl chloride concentrations could accumulate.

Another desirable feature of the system is the solid division between the floors in the building. This assures that vinyl chloride leaks on one floor will not increase employee exposure on the other floor.

The primary benefit of the system is the large quantity of air that is moved through the building (~13 air changes/hour in winter and 27 air changes/hour in summer). This supplies sufficient dilution to minimize the number and duration of vinyl chloride excursions over 5 ppm. Note that more exhaust volume is provided in the summer than in the winter. This has nothing to do with seasonal process variables; rather, it is an energy conservation method. Less airflow in winter means that less tempered makeup air is necessary and subsequently less energy is expended. It is interesting (although not satisfactorily understood) that average gas chromatograph air sampling results do not reflect an increase in the winter when less air is moved.

#### DRAWING BOARD CONTROL TECHNIQUES

##### Reactor Cleaning Frequency

The best control would of course be to modify each process such that the reactors could be kept closed for indefinite periods. Plant engineers are currently testing a system that would reduce suspension reactor opening frequency to once every 10 to 20 batches. The system includes recipe changes and the use of a dual purpose valve that will allow high pressure water cleaning and the spraying of a proprietary coating on the reactor surface without opening of the manway.

##### Process Water Disposal

Presently, process water contaminated with vinyl chloride is pumped to an outside sump. There are firm plans to recycle all process water (containing over 10 ppm vinyl chloride) through one of two proposed stripping operations.

##### Vent Gas Cleaning

A treatment system for reducing vinyl chloride concentrations (to 10 ppm) in the vent stream from the recovery system will be installed. Either a carbon adsorption or solvent absorption treatment technology will be developed.

##### Dispersion Resin Stripping Process

Shortly, a stripping process will be installed for removing residual vinyl chloride from the PVC slurry immediately after the reaction. This will minimize the potential of exposure to vinyl chloride downstream of the operation.

## EXPOSURE DATA AND CONCLUSIONS

Exposure data for process operators and maintenance employees are provided quarterly with 8-hour charcoal tube samples. A summary of the results over the past several years is presented below:

<u>Period</u>	<u>1 ppm</u>	<u>1-5 ppm</u>	<u>5 ppm</u>
1974	0	38%	62%
1975	42%	44%	14%
1976	55%	36%	9%
1977 (first half)	65%	30%	5%

The striking reduction in exposure to vinyl chloride during 1975 correlates with the time period during which most of the engineering controls were implemented. It is anticipated that, once installed, the drawing board control plans previously mentioned will drastically reduce employee exposure rate.

## PERSONAL PROTECTION EQUIPMENT

The respiratory protection program follows the requirements of the OSHA regulations for vinyl chloride and is activated by the process gas chromatograph monitoring system. Employees are required to use the half-face supplied air line system when the amber warning light (vinyl chloride reading greater than 1 ppm) is activated. This type of respiratory protection is also required when employees perform specific job tasks which are suspected of releasing vinyl chloride. A flashing red light (vinyl chloride greater than 5 ppm) also dictates the use of the half-face supplied air line system. The difference between the two alarms is that the flashing red light means that employees must use the air line respirator when moving from one air plug to another. If the monitoring system detects a vinyl chloride concentration in excess of 900 ppm, an alarm is sounded and the building must be evacuated. A self-contained air pack is required for re-entry into the building.

When employees enter a reactor to clean it, protective clothing is required to prevent skin contact with vinyl chloride contaminated liquids. The clothing includes a cotton work uniform, gloves, a head covering, impervious boots and a full-face supplied air respirator.

Work uniforms are provided daily for all employees.

## CONTROL OF OTHER POTENTIAL HAZARDS

### PVC Dust

In the suspension polymerization process, dust may become airborne at the vibrating screens and the bagging stations. Employees rarely enter the screening area and exposure to airborne dust is negligible. Control is effected by maintaining tight connections between the resin hopper and the screens, and by providing periodic clean-up using industrial grade vacuum cleaners. The suspension resin baggers are not provided with local exhaust ventilation and total nuisance dust concentrations range from 3 mg/m<sup>3</sup> to 9 mg/m<sup>3</sup>.

In the dispersion polymerization process, dust may become airborne at the grinder and at the bagging stations. The grinder is closed to the workplace and is under a negative pressure induced by the pneumatic air system for transporting the resin. Because the dispersion resin particles are much smaller than the suspension resin particles (and therefore much more likely to become airborne), the dispersion resin baggers are provided with local exhaust. The exhaust consists simply of a small canopy hood located directly over each bagger feed spout. The hood face velocity was measured at .508 - .762 m/s (100 - 150 fpm). During 1975 and 1976, 36 personal samples were collected to estimate the bagger operator's exposure to total dust. The average time-weighted average concentration was 3.6 mg/m<sup>3</sup>, which is well below the permissible limit of 15.0 mg/m<sup>3</sup> for total nuisance dust.

## Noise

Noise levels in the reactor building range from 89 dBA to 91 dBA in both the dispersion and suspension process areas. The major noise sources are the agitator motors and the recovery pumps and compressors. Employee exposure is variable and difficult to estimate because the operators alternate between process areas and the control room. Noise dosimetry data are inconclusive as to average employee exposure, ranging from 65 - 256% of the permissible 8-hour time-weighted average exposure of 90 dBA. No noise abatement control efforts were noted. An extensive noise monitoring program has been initiated to determine which job classification is more susceptible to noise exposure.

High noise levels (94 dBA) were quite common in the bagging area of the dispersion process until modifications were made in 1975. The source of this noise exposure was the exhaust blower for the bagger exhaust hoods. Although the blower is isolated from the bagging area, the high noise levels were caused by sound waves propagating through the duct work from the blower back to the hoods. The metal ducts were also transmitting blower-induced vibrations to the hoods. A commercially available silencer was placed in the duct to attenuate the noise transmitted through the duct air space. The vibrations in the duct walls were eliminated by stiffening the duct surface with a heavy exterior wrapping material (the same effect might have been achieved by decoupling the duct from the blower with a resilient material such as neoprene). Following these improvements, the noise levels at the bagging stations were reduced from 94 dBA to 80/81 dBA. However, the levels have since risen to 91/92 dBA because of resin coating on the absorption material in the duct silencer.

Noise is not a problem in the suspension process downstream of the reactor building.



## APPENDIX A.6. ABS-SAN RESIN MANUFACTURE - CASE STUDY NO. 6

### PROCESS SUMMARY

The input materials for the ABS resin manufacturing process are acrylonitrile, butadiene and styrene along with a small amount of a solution containing emulsifiers, catalysts and modifiers. As indicated in the block diagram in Figure A.6-1, the polymerization is carried out in three stages. In the first stage, the butadiene and styrene are mixed with a catalyst, emulsifier and modifier, and then copolymerized to form a low molecular weight styrene-butadiene polymer. The polymer formed in the first stage serves as a "back-bone" for the addition of acrylonitrile and styrene chains during graft polymerization in the second stage. Acrylonitrile and styrene are mixed with an emulsifier and catalyst and copolymerized in the third stage to form a resin.

The outputs from the second and third stages are mixed with color stabilizers and blended. The latex from the blending operation is mixed with a flocculent and forms a slurry. The slurry is filtered and washed by reslurrying prior to drying. The dried material is stored in bins for future transfer to the compounding plant.

The flow sheet shown in Figure A.6-2 gives more details about some of the blocks in Figure A.6-1. Some of the process operations carried out in the various functional blocks are clustered in the same plant area for convenience. For example, the premixing of modifiers and monomers and storage of emulsifiers required for each of the polymerization reactions is done on an elevated floor conveniently located above the polymerization reactors to permit gravity feeding into the polymerization reactors. Likewise, the blend and storage tanks for each of the resins are located in a common area.

Immediately following the butadiene/styrene polymerization, the liquid phase is transferred to a second vessel where the butadiene monomer is stripped when the system pressure is reduced by means of a water cooled vapor compressor. The liquified butadiene, containing traces of styrene, is transferred to storage tanks to await shipment back to the original manufacturer for refining and eventual recycle back to the ABS plastics manufacturing plant.

### TOXIC AGENTS AND HARMFUL PHYSICAL STRESSES

#### Acrylonitrile

8-hour TWA 20 ppm

An emergency temporary standard is being considered by OSHA

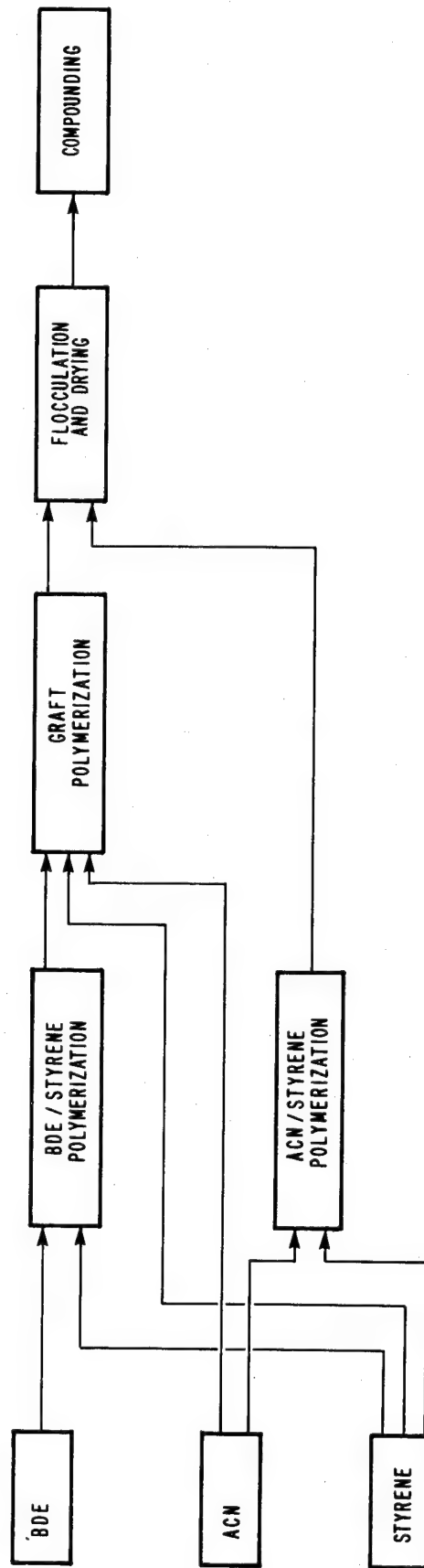


Figure A.6-1. Block Diagram - ABS Plastics Manufacturing Process

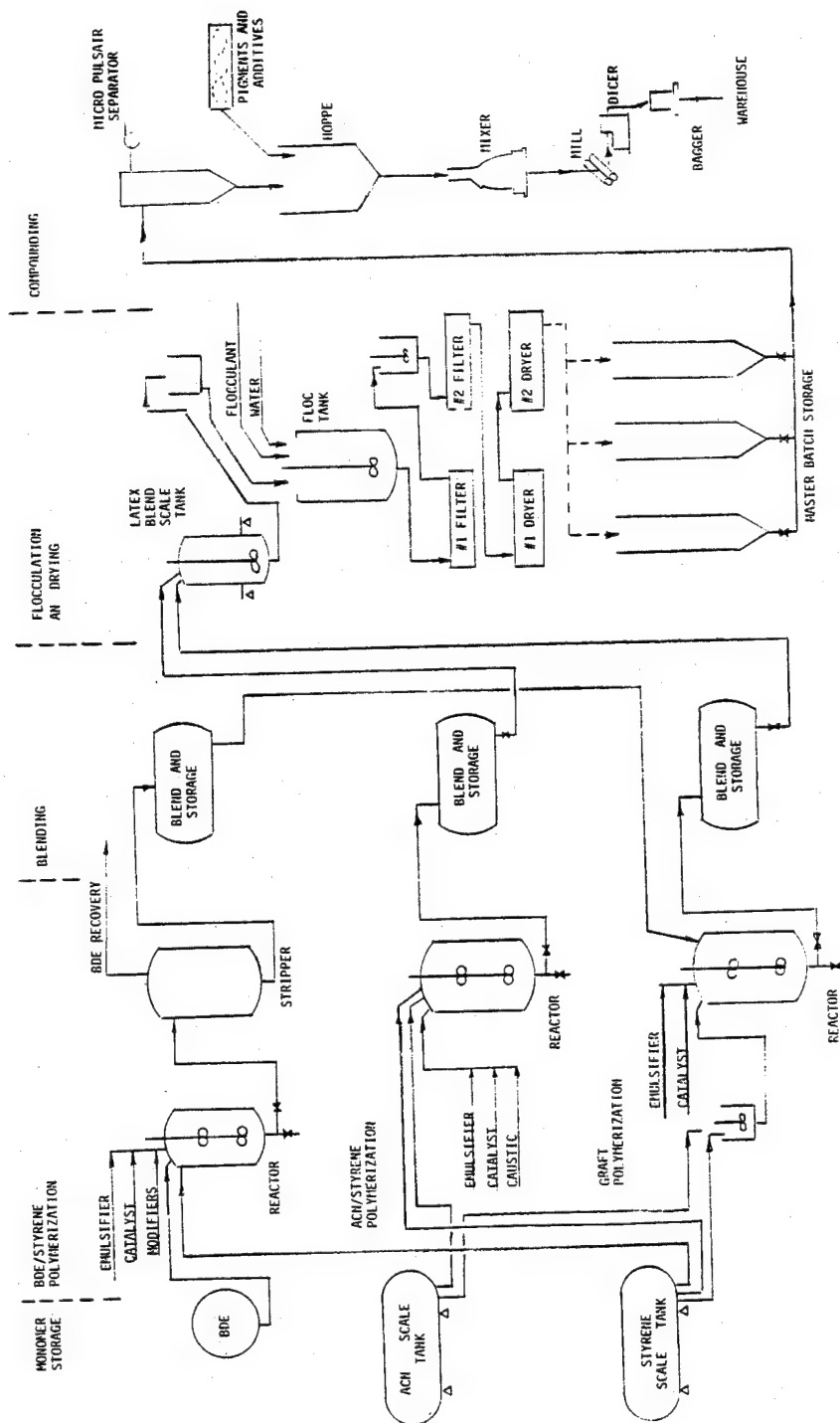


Figure A.6-2. ABS Plastic Manufacturing Process

## Butadiene

8-hour TWA 1000 ppm

## Styrene

8-hour TWA 100 ppm

Ceiling limit 200 ppm

Permissible peak 600 ppm for 5 minutes in any 3 hours

## Noise

8-hour TWA 90 dBA

## CONTROL

### Process Design, Modification and Maintenance

#### Inherent Operating Characteristics--

The unit processes from the tank farm through the butadiene/styrene polymerization and resin polymerization are totally enclosed and exposure is limited. The graft polymerization operations have a monomer mix tank provided with a readily opened manway. The acrylonitrile/styrene monomers are mixed just prior to entering the graft polymerization reactors.

#### Maintenance--

Every attempt is made to avoid hazards to workers while performing on-stream repairs in emergency situations. Routine maintenance is carried out according to approved company procedures. For example, the reactor entry and clean-out procedure requires the following:

- Pulling a vacuum to specified pressures
- Filling of reactors with water to displace all atmosphere in the reactor
- Connecting to live steam and boiling the reactor contents
- Opening and placing blinds into all entry lines
- Placing of blower to purge air
- Testing of vessel air for explosive mixtures and oxygen level prior to entry

Personnel entering vessels for any reason must wear MSA Comfo constant flow air line respirators.

## LEAK DETECTION AND PREVENTION

### Monitoring Instrumentation

A plant survey utilizing a Century OVA Analyzer for leak detection is made to determine all possible leak sources.

The system of leak detection and reporting utilizes a form and tag system. Each leak is recorded on a form and a tag and stub is used to identify the leak. The leak is tagged and the stub is given to the Maintenance Department for correction.

After the leak is repaired, another test is run to see if repairs were successful in checking the leak. In the event the leak was not corrected, the tag system is repeated until the leak is repaired.

### Important Equipment Features

A list of seals for pumps, agitators, valves and flanges is given in Table A.6-1. The more difficult applications are associated with the polymerization reactors. The reactors are equipped with double mechanical seals around the agitator shafts and piston-type valves because of the pressures involved and the tacky products that tend to stick to valve surfaces.

Table A.6-1. Seals for Pumps, Agitators, Valves and Flanges

Application and Equipment Model Number	Seal Manufacturer	Seal Model No.
Butadiene Tank Car Unloading Dayco 7276-100-2 with Dixon Interlocking Connector		P-5203 with Boss Male x GJ Female
Acrylonitrile Tank Car Unloading Dayco 7276 Hose with Quick Disconnect Coupling		Neoprene Gasket
Butadiene Charge Pumps Peerless Model DM Peerless Model CIF	Crane	Mechanical Seal "9" Carbon
Acrylonitrile Charge Pump Peerless Model DM		Mechanical Seal Durometallic
Resin Polymerization Reactor Agitator Seal Lightin-Mixer	Crane	Type #9 Double Mechanical Seal with Viton "O" Ring and Carbon, Oil Pressurized
Bottom Valve Straham Piston Type	Straham	Teflon Packing Rings
Manway Gaskets		Pressed Asbestos with Antisieze Grease
Graft Polymerization Agitator	Crane	Type #9 Double Mechanical with Viton "O" Ring and Carbon, Oil Pressurized
Bottom Valve Yarway, Piston Seatless Air Meter, Gear-Operated	Yarway	Teflon Packing Rings
Transfer Pumps Centrifugal Mission #B6528-66	Mission	Mechanical Seal, #5 Carbon
Butadiene/Styrene Agitator	Crane	Type #9 Double Mechanical Seals with Viton "O" Ring and Carbon, Oil Pressurized
Bottom Valve Yarway, Piston Seatless Air Meter, Gear-Operated	Yarway	Teflon Packing Rings

## LOCAL EXHAUST VENTILATION SYSTEM

Local exhaust ventilation is not used extensively for controlling exposure to toxic vapors, largely because the process is closed and most of the operations are located outdoors. Two systems are used as follows:

### Sample Collection Hood

Periodically, batch samples must be obtained from the reactors. A valve at the bottom of the reactor is opened and a small amount of resin is drained into the sampling vessel. Because this operation releases unreacted monomer, an exhausted sampling hood was developed to enclose the operation and remove toxic vapors away from the workers' breathing zone. None of the hoods were functioning properly during the survey, because the exhaust ducts were all clogged with dried latex. The problem is that the exhaust ducts were all located at the bottom rear of the hood, and the latex splatters into them and causes obstructions to proper airflow. This deficiency could be alleviated by positioning the duct at the rear top of the hood and providing a baffle to prevent splattering on the duct. Alternately, the present duct takeoff position would be acceptable, if a baffle was positioned over it. The exhaust system is designed to provide a hood face velocity of 150 fpm across the front of the hood.

### Floc Pots

The latex from the blending operation is pumped to a heated, agitated floc pot where flocculents and water are added and the latex flocculates into a slurry form. The floc pots are partially closed at the top and provided with local exhaust ventilation as depicted in Figures A.6-3 and A.6-4.

The system has a rated airflow capacity of  $1.89 \text{ m}^3/\text{s}$  (4000 cfm) or  $0.472 \text{ m}^3/\text{s}$  (1000 cfm) for each floc tank. It is doubtful that the system, as operating, is moving  $0.472 \text{ m}^3/\text{s}$  (1000 cfm) from the tanks, because the flexible connectors were not tight and tank tops were not secure. The system design is good and would be very effective with minor maintenance modifications. Further improvements are being made by isolating each set of floc pots with its own ventilation system.

## GENERAL VENTILATION SYSTEM

Process equipment up to the flocculation operation is located outdoors and mechanical general ventilation is obviously not necessary. There is, however, a control room containing the process control panels. The control room is pressurized via an independent air system with a particulate filter. Employee exposure is essentially zero in this area.

The flocculation building contains two sets of four floc pots, four large filters and four large dryers. All of this equipment produces a significant heat load and the general ventilation system is primarily designed to provide sufficient air movement to remove this heat. The placement of the exhaust fans is based on this consideration rather than concern for dilution and removal of airborne toxicants. The total system provides an airflow of  $53.8 \text{ m}^3/\text{s}$  (114,000 cfm), and the volume of the building is estimated at  $68.9 \text{ m}^3$  (146,000 cubic feet). Thus, the airflow rate is approximately forty-six air changes

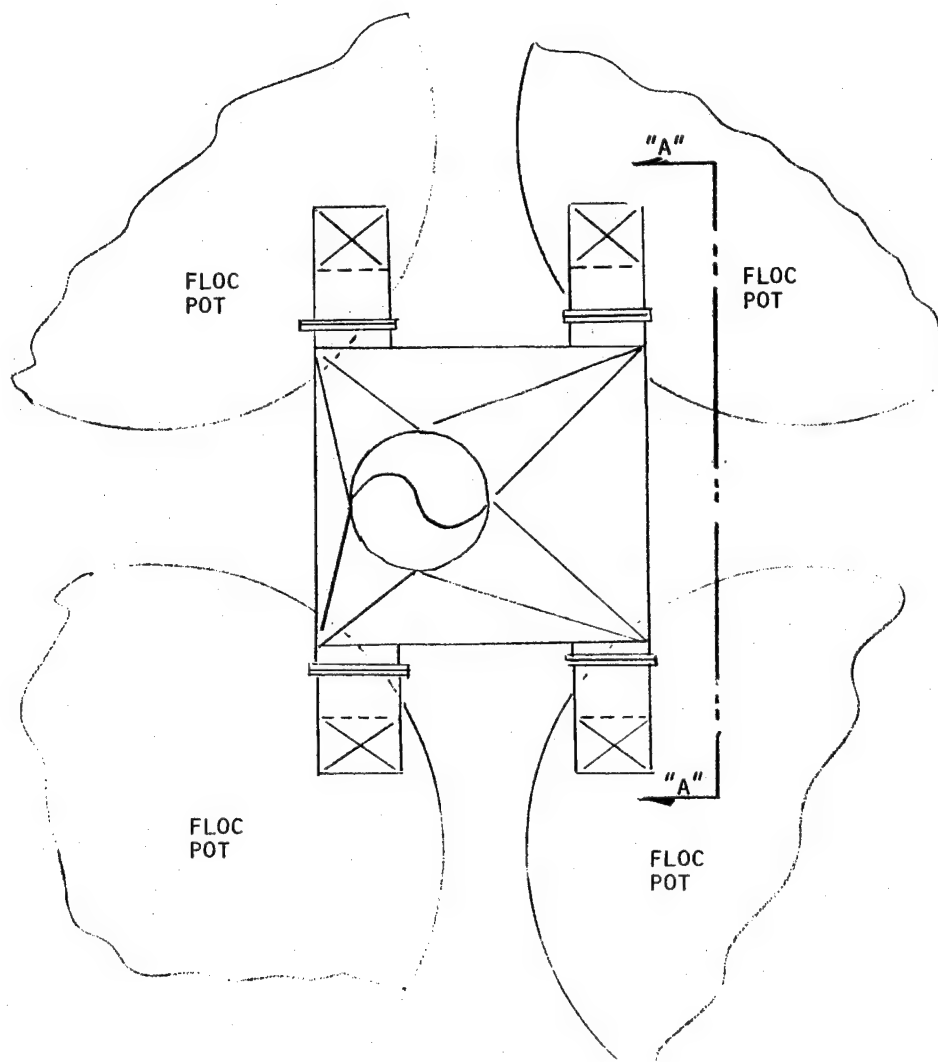


Figure A.6-3. Top View of Floc Pot

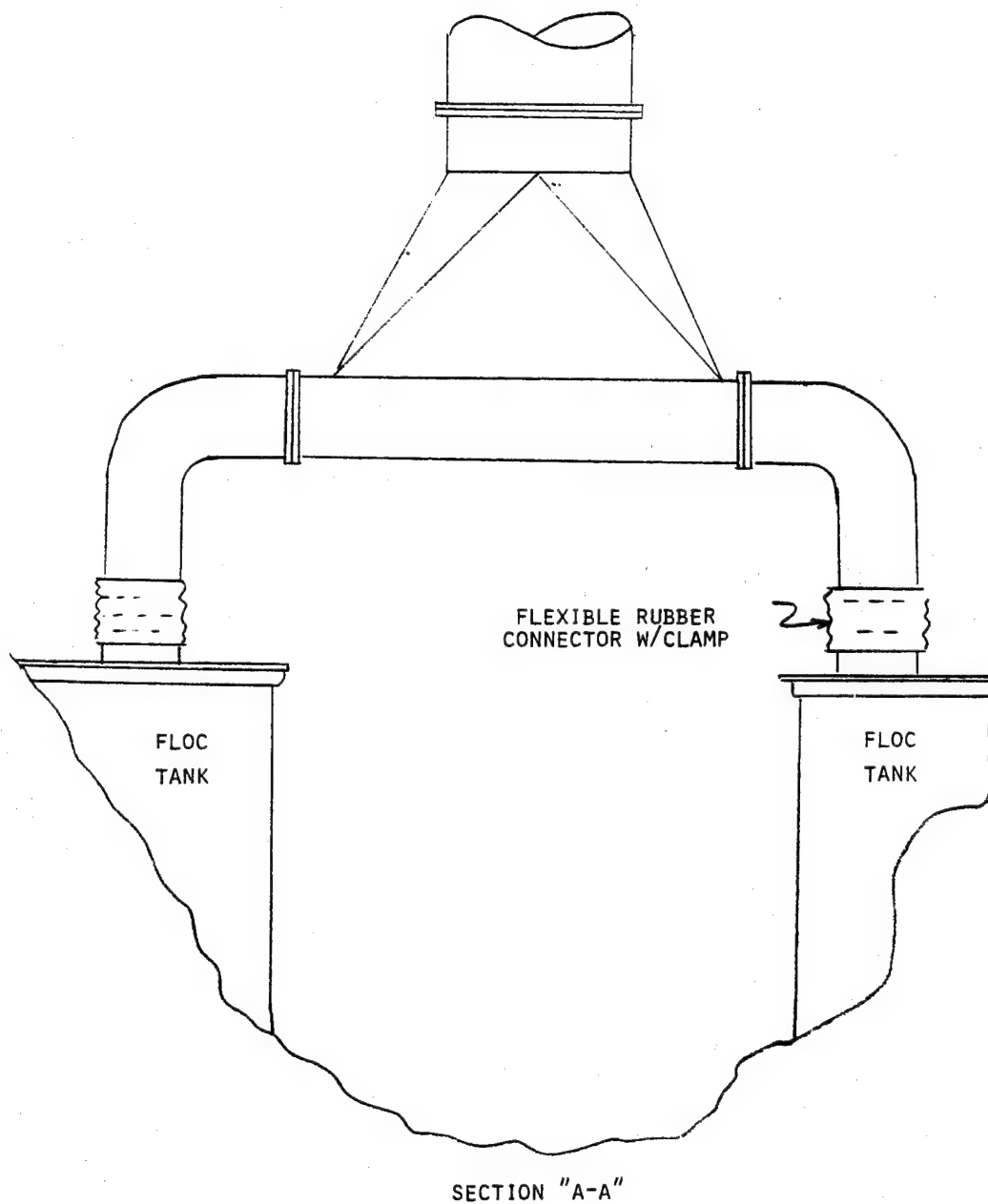


Figure A.6-4. Sectional View A-A of Floc Pots shown in Figure A.6-3



per hour. This very rapid change of air undoubtedly assists in minimizing concentrations of styrene and acrylonitrile vapors.

#### EXPOSURE DATA AND CONCLUSIONS

Area samples using gas detector tubes, charcoal tubes and a Miran IA portable spectrophotometer have been collected since 1975 to measure workplace concentrations of acrylonitrile and styrene (butadiene sampling has been limited due to its high permissible exposure limit of 1000 ppm). On a routine basis, personal samples are collected and have been used to estimate employee exposure. A combination summary of plant and survey area sampling data is presented in Table A.6-2.

Table A.6-2. Area Sampling Data

Location	Average Sample Results		Comments
	Acrylonitrile	Styrene	
Monomer Mix Room	3.6 ppm (17)*	2.0 ppm (5)*	Not a normal work area; samples taken in general room areas; peak sample result of 30 ppm acrylonitrile; tanks are closed and vented to the atmosphere
Reactor Area	9.5 ppm (8)*	0.5 ppm (2)*	General area samples; many taken with reactors open for cleaning
Flocculation Building	3.5 ppm (16)*	2 ppm (2)*	All samples taken in floc pot area near operator's desk and control panel
Tank Farm Storage	1.2 ppm (12)*	-	General area samples

\*Number in parentheses indicates number of samples.

Workplace concentrations of styrene vapor are negligible relative to the current permissible exposure limit of 100 ppm. Although a few measured concentrations are excessive, average workplace concentrations of acrylonitrile are well below the current permissible exposure limit of 20 ppm.

Some measurements (Table A.6-3) of styrene and acrylonitrile using the portable spectrophotometer are interesting because they illustrate the effect of different resin batches and, in one case, the effectiveness of the floc pot local exhaust.

It is not known whether the fluctuations in vapor concentrations are due totally to the different resins, or to operating conditions, during the changeover from one resin to another. It is probable that the fluctuations are due to a combination of both factors. These data assist in explaining the relative high acrylonitrile concentrations seen from the area and personal sampling data. The rapid dissipation of vapors following a change in resin indicates a very effective general exhaust system.

The second set of data shows a degree of control effectiveness produced by the floc pot local exhaust system. Average acrylonitrile concentrations increase from 7 ppm to 25 ppm when the exhaust is shut down. When the system is activated again, the concentration goes back down from 25 ppm to 4 ppm. The average acrylonitrile concentrations (7 ppm and 4 ppm), when the exhaust is running, demonstrate that there are either leaks from the floc pots or there are separate sources of vapor escape in the area.

Table A.6-3. Area Sampling Data - Flocculation Building

Location	Toxicant	Time Period	Results		Comments
			Range	Average	
Between two floc pots, 10' from control panel	Styrene	3:50 pm - 11:50 pm	0	0	Resins A and B
Between two floc pots, 10' from control panel	Styrene	11:50 pm - 12:40 am	20-55 ppm	35 ppm	Changed resin B to resin C
Between two floc pots, 10' from control panel	Styrene	12:40 am - 6:55 am	0	0	
Between two floc pots, 10' from control panel	Styrene	6:55 am - 7:00 am	35-150 ppm	75 ppm	
Between two floc pots, 10' from control panel	Styrene	7:00 am - 8:37 am	0	0	
Between two floc pots, 10' from control panel	Acrylonitrile	8:40 am - 10:03 am	4-10 ppm	7 ppm	Resins A and C
Between two floc pots, 10' from control panel	Acrylonitrile	10:03 am - 10:13 am	7-65 ppm	25 ppm	Resins A and C, local exhaust for floc pots turned off
Between two floc pots, 10' from control panel	Acrylonitrile	10:20 am - 10:40 am	0-8 ppm	4 ppm	Exhaust turned back on

During the survey, personal sampling devices were worn by two reactor operators and the flocculation building operator for four separate periods of about 2 hours each during 2 consecutive days. The results are summarized in Table A.6-4.

Table A.6-4. Personal Sampling Data

Job Classification	Sample Results	
	Acrylonitrile	Styrene
Reactor Operator #1		
First Day	0.25 ppm 1.4 ppm	0.05 ppm 0.3 ppm
Second Day	1.3 ppm 2.2 ppm	1.7 ppm 0.5 ppm
Reactor Operator #2		
First Day	<0.032 ppm 8.0 ppm	<0.01 ppm 0.5 ppm
Second Day	0.2 ppm 3.6 ppm	0.2 ppm 0.3 ppm
Flocculation Building Operator		
First Day	14.0 ppm 3.1 ppm	3.1 ppm 0.85 ppm
Second Day	3.4 ppm	0.28 ppm

The results are highly variable, as would be expected (for example, reactor operator #2 received almost no exposure to acrylonitrile during the morning, and an average exposure of 8 ppm during the afternoon). This is not surprising because the operators alternate between non-exposure areas such as the control room and exposure areas such as the reactors. To complicate situations, the exposure while in process areas depends on such factors as reactors being open for cleaning, leaks in process equipment, sample taking, etc. A rigorous personal sampling program has been developed to gather significant data to truly characterize employee exposure. Personal data has been established on all operators working in polymerization, finishing and latex handling jobs. Data has been obtained on laboratory technicians, tank farm operators, mill operators, banbury operators, pigment operators (east side) and maintenance personnel working in the polymerization area.

Table A.6-5. Summary of Acrylonitrile Data - August 1977

Reactor Area		Peak	TWA
Reactor Operators	High	16.8	8.5
	Average	-	1.2
Floc/Blend Latex Handler	High	60.8	14.2
	Average	-	5.8
West Floc (Finishing) Operator	High	9.0	3.7
	Average	-	2.4
East Floc (Finishing) Operator	High	4.2	2.2
	Average	-	1.3
Laboratory "A" Technicians	High	5.4	1.4
	Average	-	.5
East Compounding	Average	-	0.8
West Compounding	Average	-	.11
Tank Farm Operator	Average	-	.19
Cleaning Reactor	Average	-	7.0

This data was obtained by taking 15-minute samples in sets of six. The data presented above is an average of the TWA value obtained by averaging the TWA for each set of samples. A total of 70 sets (435 individual samples) were taken.

Several procedural and equipment changes have been made and results and data indicate reductions in exposure to organic vapors (acrylonitrile and styrene).

- Personnel sampling program yields 25 to 30 sets of data per week (150 to 180 samples).
- A detailed list of job functions has been developed which requires the use of air line or cartridge respirators.
- Projects have been proposed to further eliminate or reduce exposures (sampling methods, engineering studies, etc.).

Two job tasks have been of particular interest to plant personnel due to a high potential for exposure. These tasks are reactor cleaning and sample taking. Respirators are worn by employees while cleaning the reactors and/or sample taking. Personal samples for employees involved in these tasks were collected during the survey and results are presented in Table A.6-6.

Table A.6-6. Personal Sample Data for Selected Tasks

Job Task	Personal Sample Result		
	Butadiene	Styrene	Acrylonitrile
Cleaning Reactor	7.0 ppm	14.0 ppm	-
Cleaning Reactor	-	8.6 ppm	0.53 ppm
Cleaning Reactor (on scaffold in reactor away from manway)	-	2.9 ppm	17.5 ppm
Cleaning Reactor (on scaffold in reactor, close to manway)	-	4.7 ppm	1.3 ppm
Reactor Sampling (5 reactors)	183.5 ppm	0.6 ppm	-
Monomer Mix Room Sampling	-	4.5 ppm	0.82 ppm

Although these data are limited and far from conclusive, it is apparent that employee exposure during these tasks is greater than exposures encountered overall, but it is also probable that exposures are not excessive during these tasks. Exposures while sampling reactors will be greatly reduced when the exhaust hoods are repaired and modified.

#### PERSONAL PROTECTION EQUIPMENT

Personnel entering vessels for any reasons must wear MSA Comfo constant flow airline respirators. Personnel in other job classifications are required to wear MSA Comfo II cartridge respirators equipped with GMA-organic vapors cartridges when performing certain functions.

- Reactor operator - while sampling reactors and monomer mix tanks
- Latex-A operator - while sampling blend tanks and venting strainers
- Finishing-A operator - while working around floc pots, open troughs and filters
- Maintenance personnel - when blinding off or buttoning up resin or graft vessels or while changing strainers
- Tank farm operator - except when unloading AN car other than tank car standpipe

## CONTROLS FOR OTHER POTENTIAL HAZARDS

### Noise

Employee exposure to noise in the reactor area is not excessive because 1) operators spend much time in the control room and, 2) noise levels throughout the area are not very high (around 85 dBA on the mezzanine around the reactor tops and 90 to 92 dBA on ground level around the reactor bottoms). The primary sources of noise are the reactor agitator motors, the pumps on ground level and the circulating water pump line where live steam is injected into a cold water line. Low-noise steam/water mixing injectors are being evaluated. Employees are not required to wear ear plugs or muffs.

Noise levels in the flocculation building are excessive (ranging from 88/90 dBA at the control panel to 90/92 dBA in other process areas). The primary sources of this exposure are the floc pot agitator motors, the slurry pumps, the duct axial blower for the floc pot exhaust system (located in the duct, 10 feet above the pots), primary and secondary discharge blowers and the dryers (due to steam leaks and discharges). No engineering controls were observed inside the floc building. Employees are required to wear ear protection inside the building.

The floc line primary discharge blowers are very noisy (97/102 dBA) and, although they are outside the building, they contribute to employee exposure throughout the area. The discharges for many of these blowers have been muffled with standard, commercially available muffler units. In addition, the secondary blowers and a large vacuum pump were acoustically enclosed. The beneficial effects of the mufflers and enclosures are demonstrated in Table A.6-7.

### PLANNED OR ONGOING IMPROVEMENTS

#### Monitoring Network

The plant management is planning to install an instrument system for automatically monitoring worker exposure to hazardous materials and for providing adequate warning to operators and maintenance personnel in case of equipment malfunction or process upsets. The plant engineers are reviewing instrument systems that would be suitable for their needs.

#### Sampling of Process Streams

A program is underway to reduce the potential for worker exposure when operators collect grab samples of process streams. Certain process streams are difficult to sample since they are tacky and tend to clog sampling ports and containers. Special sampling equipment is being evaluated for these applications.

#### Elimination of Open Mixing Tanks

Plans are underway to replace the monomer mix tanks with in-line metering and mixing of input materials entering the polymerizers. The existing mix tanks are provided with manways and exhaust ventilation. However, due to occasional

oversight by the operators, the manways are not always closed properly after sampling of the process stream.

Table A.6-7. Noise Survey Results - Flocculation Building

Location	Noise Level (dBA)			
	A*	B*	C*	D*
1st Level-West of #1 and #2 Vacuum Pump	105	102	102	97
1st Level-North and East of #2 Secondary Blower	-	102	93	92
1st Level-North and West of #1 Secondary Blower	102	101	94	92
1st Level-North of Secondary Floc Line Blower #1 and #2	100	100	94	96
1st Level-Base of South Stairs	-	97	92	89
1st Level-1st Landing South of Stairs	98	100	91	89
2nd Level-Between #1 Line Filters North of #3 Panel Board	93	94	93	91
2nd Level-East Side of #4 Line Panel Board	93	92	91	90
2nd Level-Outside North Door	<90	85	83	83
1st Level-East of #2 Primary Blower	104	96	97	92
1st Level-West of #1 Vacuum Pump West of #2 Primary Blower	102	95	96	97
1st Level-East of #1 Primary Blower	103	96	97	96
1st Level-West of #1 Primary Blower	102	95	96	95
2nd Level-At Work Desk Area Line #1 and #2, Outside North Door	92	92	91	90
	-	89	88	86
2nd Level-South of Latex A Panel Board	91	89	87	87

\*Conditions: A - Noise readings prior to start of work.  
 B - Noise readings after mufflers installed on #1 and #2 line primary blowers.  
 C - Noise readings after mufflers installed on #1 and #2 secondary blowers.  
 D - Noise readings after acoustical enclosures installed on #1 and #2 line secondary blowers and #3 vacuum pump.

## APPENDIX A.7. POLYSTYRENE PROCESS - CASE STUDY NO. 7

### PROCESS SUMMARY

Polystyrene is produced by holding styrene monomer in an enclosed reactor and subjecting it to progressively increasing temperatures. The flow sheet in Figure A.7-1 is for a polystyrene process employing two parallel batch reactors that provide an essentially continuous flow of polystyrene to the rest of the process. The temperature control within the polymerization reactors is maintained by means of oil circulating through internal heat exchanger tubes.

When the polymerization is completed in a reactor, its contents are transferred by means of a gear pump to a holding tank. The polystyrene stream containing some styrene monomer is continuously sprayed into a devolatilizer to flash vaporize the unreacted styrene. The styrene monomer is condensed and pumped out to a slop tank. A vacuum pump operating downstream of the condenser removes the inert gases along with small amounts of styrene and vents the gas mixture to the outside stack.

The devolatilized polystyrene is pumped through an extruder die head where a large number of small diameter threads are formed. The polystyrene threads are cooled by passing through an open tank of cooling water. The water droplets clinging to the solidified threads are blown away by jets of air. The threads of polystyrene are cut into small pellets in a Cumberland pelletizer. The pellets are screened to remove oversize particles and conveyed to a hopper for bagging or for air conveyance to silos for bulk shipment by truck or carload.

### TOXIC CHEMICAL AGENTS OR HARMFUL PHYSICAL STRESSES

#### Styrene

8-hour TWA 100 ppm  
Ceiling limit 200 ppm  
Peak level 600 ppm for 5 minutes in any 3 hours

#### Noise

8-hour TWA 90 dBA

### CONTROL TECHNIQUES

#### Process Design

The process is totally enclosed from the tank farm to the extrusion die head. The tank farm and the reactors, holding tanks and devolatilizers are located

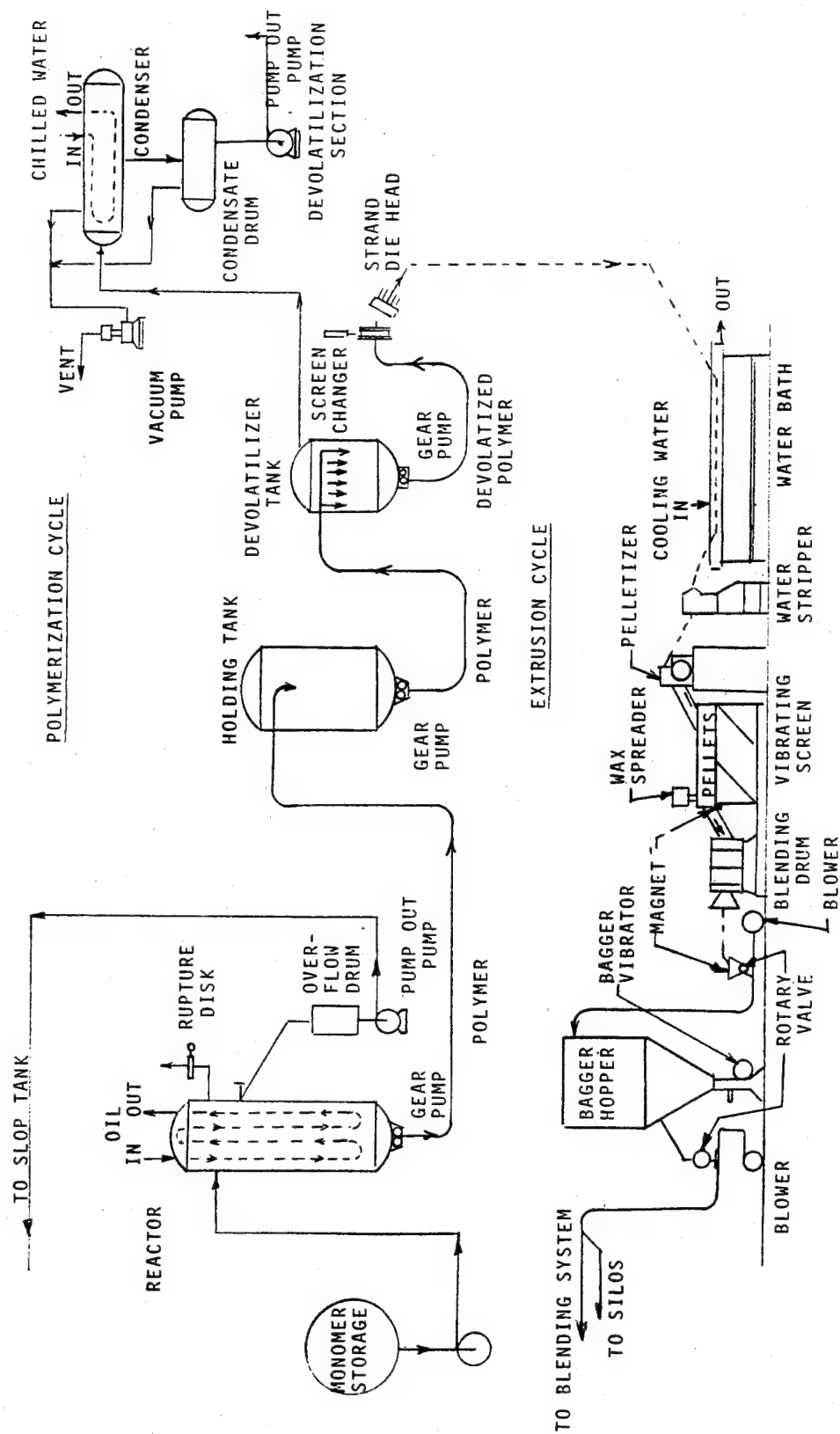


Figure A.7-1. Polystyrene Process Flow Sheet



outdoors. The extruding and pelletizing operations are located in a warehouse.

### Important Equipment Features

The plant is of a more recent design and the process equipment used is adequate to meet the federal regulations for exposure to styrene. A list of process equipment and points of applications within the process is given in Table A.7-1.

Table A.7-1. Seals for Pumps and Valves

Item and Area of Application	Seal Manufacturer	Seal Model No.
Pumping Molten Styrene Gear Pump Johnson Machine Works Model JMTW-1722-H	Crane	Style C-06
Pumping Styrene Monomer Demning Co. (end suction, double bearing, enclosed impeller centrifugal pump)	Durametallic	Mechanical Seal Dura-Seal ES5-TT
Vacuum Pumping Styrene Kinney Vacuum Pump Co. Model KDH-150	Kinney	Silicone Grease
Styrene Slops Baldor Baldor Baltic Line	Durametallic Chesterton	Mechanical Seal
Styrene Pipeline Valves Powell Valve Co.	Crane	Style C-06
Manways on Reactors	Black, Sivalis and Bryson	Monel "6" Type RV Ankorite 450 (around manways not pressurized) Ankotalllic (for pressure vessels)

### LOCAL EXHAUST VENTILATION SYSTEM

The process is completely closed and located outdoors from the tank farm to the extrusion die head, and thus, local ventilation is not required. From the extrusion die head, the hot resin strand falls into a long water batch preceding the pelletizer. Steam and a small amount of styrene are liberated and must be removed from the workplace. This is accomplished with a simple canopy hood positioned directly over the extrusion die head. A hood face velocity of approximately 150 fpm is provided. The canopy hood is baffled on two sides to prevent cross-currents from interfering with vapor removal. The effectiveness of the hood is demonstrated by taking detector tube samples for styrene inside and outside of the hood. The samples showed styrene concentrations of 15 ppm in the steam cloud entering the hood, and zero directly outside of the hood.

## GENERAL VENTILATION SYSTEM

As previously mentioned, the reaction area is located outdoors and any escaping vapors are effectively diluted and dispersed by natural ventilation. The warehouse containing the extrusion, pelletizing and bagging operations is not provided with any mechanical general ventilation. The air in the warehouse is circulated and replaced via natural ventilation through openings in the structure.

## EXPOSURE DATA AND CONCLUSIONS

Personal and area charcoal tube samples for styrene were collected during the survey. The results are presented in Table A.7-2.

It is obvious that employee exposure to styrene is negligible relative to the permissible exposure limit of 100 ppm. This is due to the closed nature of the process, the fact that most of the process is outdoors, and the effectiveness of the extruder die head canopy hood.

Table A.7-2. Personal and Area Samples for Styrene

Employee or Sample Location	Results (ppm styrene)*
Operator #1, Outside Cleaning and Loading Monomer	0.04 0.01 0.01
Extruder Operator	<0.01 0.22 1.71
Operator #2, In Warehouse and Outside in Reaction Area	0.02 0.03 <0.02
At Extruder Work Desk	0.05 <0.01

\*Each set of three personal samples (first three items cited) was collected consecutively for approximately 4 hours during the work shift.

## NOISE CONTROLS

Noise levels are low in the reaction area, ranging from 83 dBA to 87 dBA. The principle sources of noise are pumps and various motors.

There is a significant noise exposure throughout the warehouse building. Area sound levels around the process line are shown in Figure A.7-2.

The high noise levels in the process area result from numerous sources including the air dry knife, the compressors, the screen, the tumbler, the bagger and particularly the pelletizer (Cumberland 8", Model No. 64050). The pelletizer has been acoustically enclosed using quick-opening acoustical panels (information on the enclosure is available from the manufacturer, Cumberland Engineering Company). It is difficult to gauge the effectiveness of the enclosure because the panel fittings were not tight and the surrounding noise sources (particularly the pelletizers on two other process lines which have

yet to be enclosed) tend to mask any potential reduction in noise levels at the enclosed pelletizer. The noise level increases from 97 dBA to 103 dBA when the panels are removed. The panels have sufficient mass to provide the desired transmission loss and there is also sufficient internal absorption material to prevent reverberant build-up. However, it is judged that the openings to the enclosure are too large to provide optimum attenuation. No other engineering control methods for reducing noise levels were noted. Ear muffs or plugs are required in the process area.

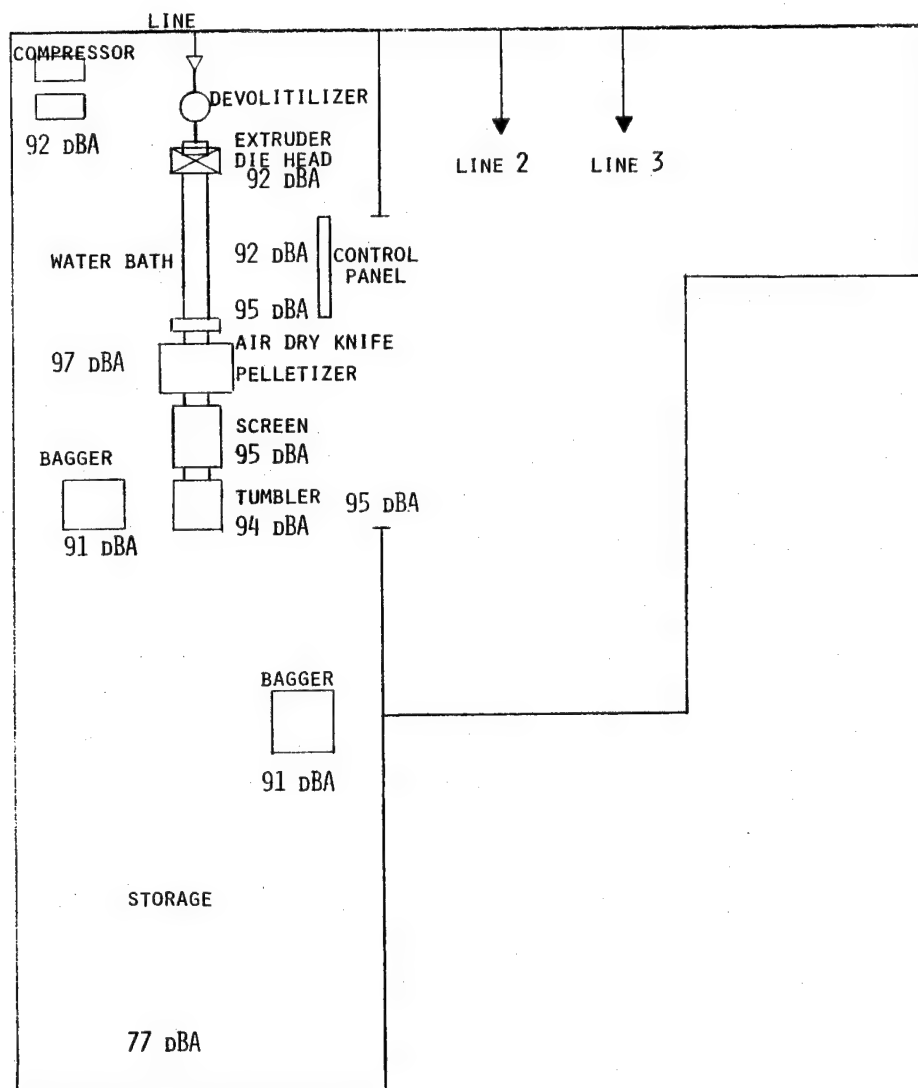


Figure A.7-2. Area Noise Levels - Process Area

## PERSONAL PROTECTION PROCEDURES

Due to the low styrene concentrations during normal operation of the plant, respirators are seldom required. The reactors and other process vessels do not have to be entered. Chemical cartridge respirators for protection against organic vapors are available for use during maintenance or other operations where high concentrations of styrene may occur. In the event of an emergency, supplied air respirators are available for use.

## APPENDIX A.8. STYRENE BUTADIENE RUBBER EMULSION POLYMERIZATION PROCESS

### CASE STUDY NO. 8

#### PROCESS SUMMARY

The emulsion polymerization process for manufacturing styrene butadiene rubber (SBR) is depicted in Figures A.8-1 and A.8-2. The process is continuous.

Butadiene is pumped from spherical and horizontal storage tanks into a surge tank in the reactor area. Styrene is pumped from vertical and horizontal storage tanks into a surge tank located outside of the reactor building. From the surge tanks both raw materials are metered into a closed, agitated reactor at a fixed rate. An aqueous solution, containing certain activators and emulsifiers made up in a pigment area, is also metered into the reactor at a fixed rate. The reactors (up to 16 in number) are arranged in series such that the reactor mass is continually exiting one reactor at the bottom and entering the next at the top. Each reactor is maintained at the prescribed temperature by ammonia coils immersed in the reacting mass. As the slurry exits the final reactor in the series, about 60% of the slurry has been polymerized. The reaction is stopped by the addition of a "short stop" agent.

From the last reactor, the slurry is pumped into a blow down tank at 110°F to facilitate monomer recovery. The slurry is pumped from the blow down tank through a pressure flash tank, a vacuum flash tank for butadiene and a large stripping column for styrene, in which unreacted butadiene and styrene are removed and recovered. The stripped latex is pumped from the stripping column into an open latex storage tank located outside the coagulation area.

The latex is pumped from the storage tank to a latex blend tank, and is continuously fed through two small, agitated tanks where an oil emulsion, an antioxidant emulsion and a carbon black slurry are added. These additions are made up in the pigment area mentioned above. The latex next flows into the coagulation tank, where brine is added and the rubber particles are agglomerated and the latex consistency is changed from a mobile liquid to a heavy cream. In the next tank, a dilute acid is added to break the emulsion and the globules agglomerate to form crumbs of rubber. The crumbs are screened, washed and dewatered on a rotary vacuum filter. The dewatered crumb is broken up in a hammermill and is air conveyed to the top of a hot air, conveyor-type dryer. The dried crumb is compacted and baled.

#### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

##### Styrene

8-hour TWA - 100 ppm  
Ceiling concentration - 200 ppm

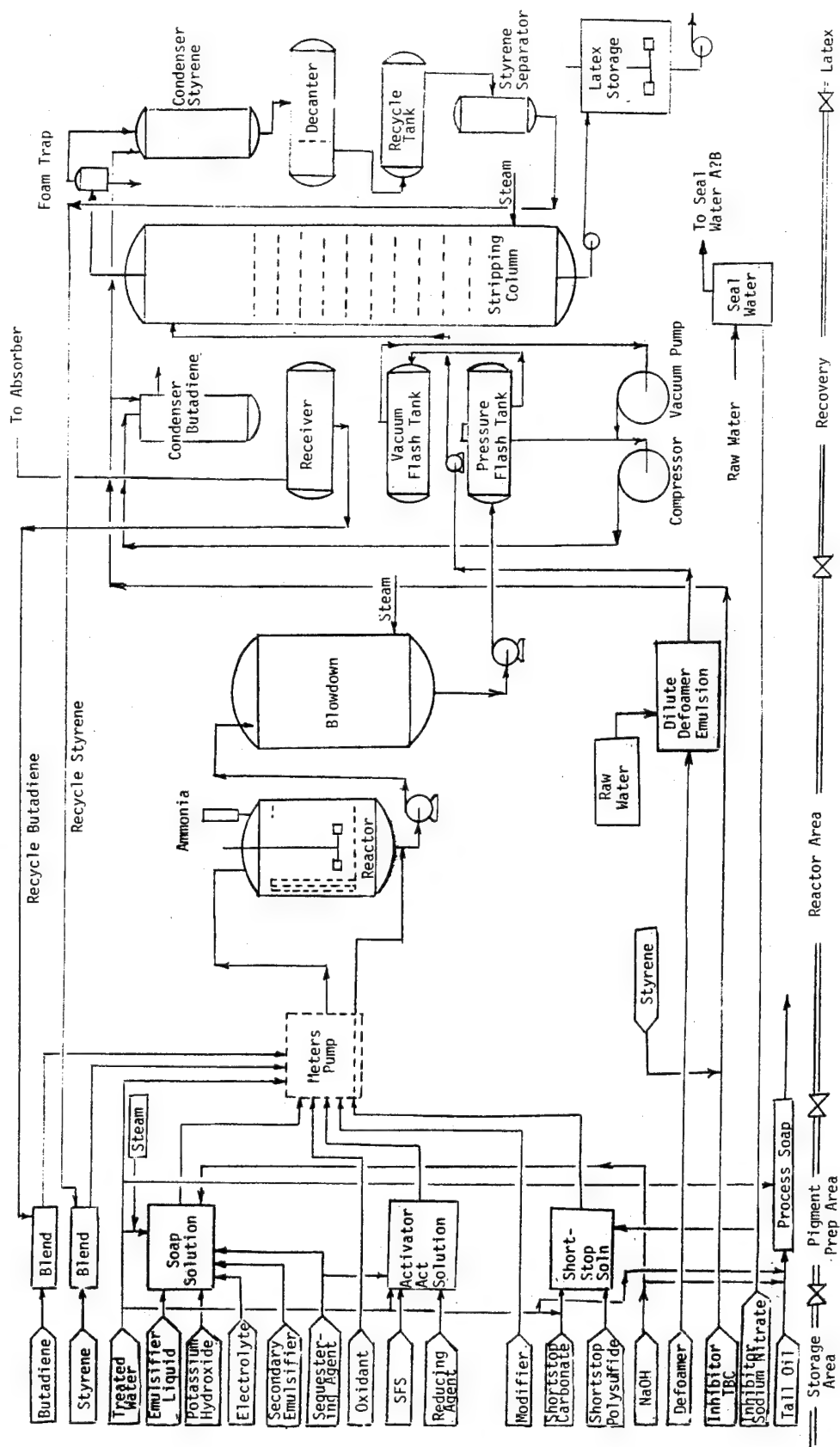


Figure A.8-1. Copolymer Plant Flow Sheet - Polymerization Area

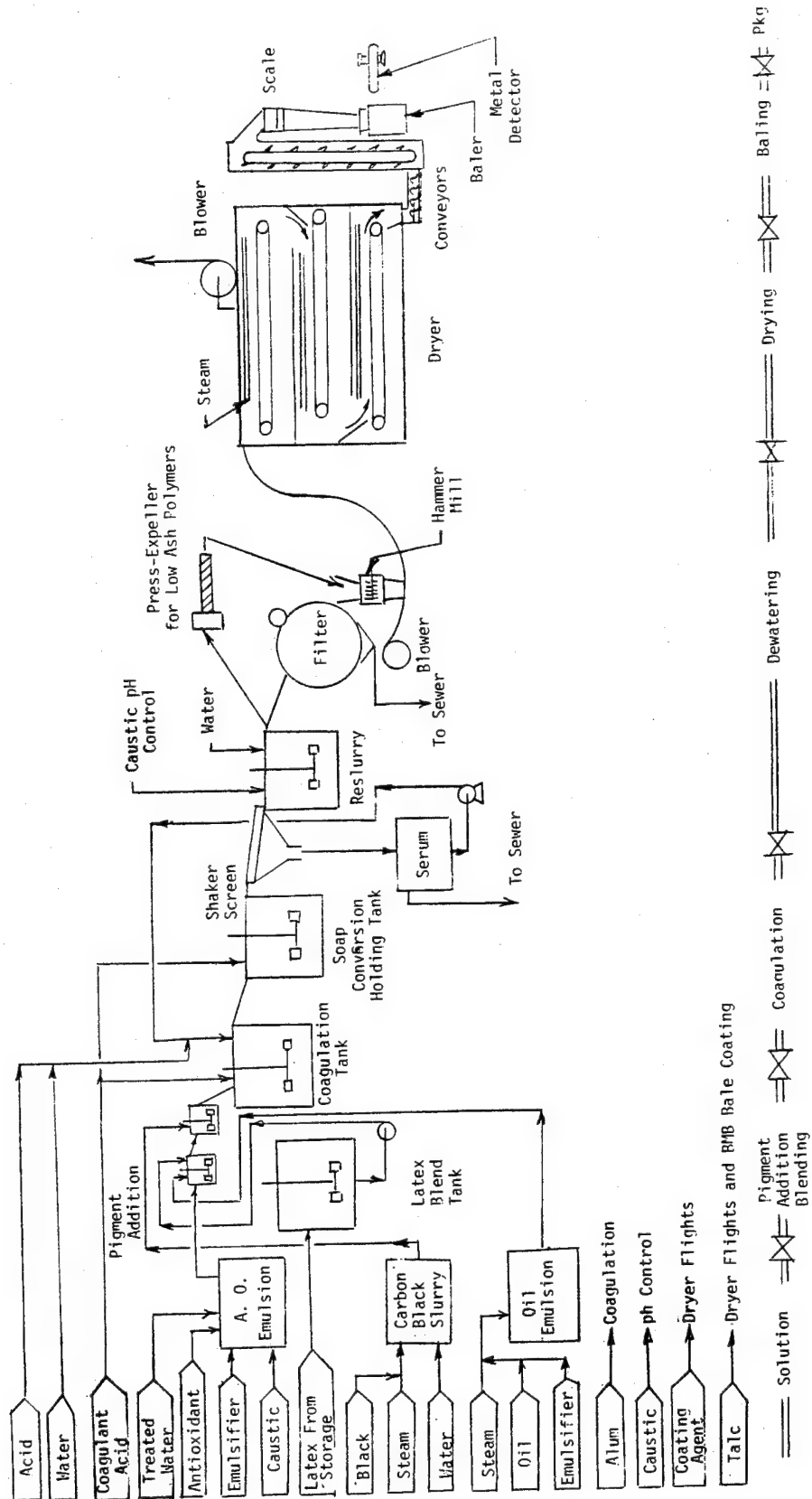


Figure A.8-2. Copolymer Plant Flow Sheet - Process Area

Peak level - 600 ppm for 5 minutes in any 3 hours

#### Butadiene

8-hour TWA - 1000 ppm

#### Benzene

8-hour TWA - 10 ppm

Ceiling concentration - 25 ppm

Peak level - 50 ppm for 10 minutes

OSHA has issued an emergency temporary standard for benzene reducing the permissible time-weighted average exposure to 1 ppm or 5 ppm averaged over any 15-minute period.

#### Minor Ingredients--

The number and complexity of minor ingredients added to the process is staggering. The broad groups of ingredients include emulsifiers, sequestering agents, oxidants, reducing agents, modifiers, defoamers, inhibitors, oils, coagulants, antioxidants, caustics and coating agents. Most of these ingredients do not have established permissible exposure limits and only limited toxicological data is available. For this reason, the controls for these materials will be discussed generally as a group.

Talc-- 8-hour TWA (nonasbestos-form) - 20 million particles per cubic foot (mppcf). Studies have shown that talc used in the process is nonasbestos-form.

#### CONTROL TECHNIQUES

##### Butadiene and Styrene Storage and Handling

Butadiene is received through pipelines into closed storage tanks under 35 psi butadiene pressure. From the storage tanks to the reactors, the system is closed, and there is very little potential for leaks.

Styrene is received by tank car and pumped into closed storage tanks which are vented to the atmosphere. There may be styrene escape when the storage tanks are filled, either from the hoses or from the vent. From the storage tank to the reactor the system is closed and leaks are uncommon.

The following area and personal sampling data demonstrate that this section of the process is well controlled and not a significant source of employee exposure:

<u>Location</u>	<u>Area Samples</u> <u>No. of Samples</u>	<u>Average Concentration (ppm)</u>		
		<u>Styrene</u>	<u>Benzene</u>	<u>Butadiene</u>
Styrene Pump House	17	14	ND*	1.34
Unloading Station	1	0.40	ND*	0.08
Main Pump House	5	7.81	ND*	2.68

\*ND indicates no benzene concentrations greater than 0.1 ppm were detected using procedure SDS #311 specified in NIOSH Manual of Sampling Data Sheets, DHEW Publication No. 77-159.



### Personal Samples

	<u>No. of Samples</u>	<u>Average Concentration (ppm)</u>		
		<u>Styrene</u>	<u>Benzene</u>	<u>Butadiene</u>
Employee A	1	.51	-	4.48
Employee B	2	1.70	ND	3.90
Employee C	4	3.83	ND	1.24
Employee D	3	1.93	ND	0.92
Employee E	2	3.10	.16	.162

### Reaction and Monomer Recovery Area

The reactors are totally closed and, since the process is continuous, they do not have to be opened except for cleaning. Each reactor is equipped with a rupture disc set for 125 psi (pressure or vacuum). The rupture discs are hooked to a flare. The blow-down tank is also totally enclosed to the workplace, and it is not opened except for very rare cleaning operations.

The reactors have to be cleaned on an average of once per year (ranging from once every 4 years for the first reactor to every 300 hours for the final reactor in the series). The cleaning procedure is as follows:

- (1) Recovery compressors pull a vacuum on the reactor
- (2) The reactor with blinds inserted into connecting piping is filled with toluene and agitation is begun
- (3) The reactor is left under heat for up to 6 hours
- (4) Toluene is flashed off to the flare
- (5) Blinds are removed and the reactor is filled with water
- (6) Water is then evacuated
- (7) Manway is opened and cleaned with high-pressure water at 10,000 psi

This procedure eliminates the need for employees to enter and manually clean the reactor. In the past, workers entered the reactor and used piano wires to remove the residual rubber. Four personal samples were collected and analyzed for toluene: time-weighted average exposures ranged from .12 ppm to 3.4 ppm.

Every 2 hours, a butadiene sample is collected in a sample jar off the end of the last reactor through a plug valve. The operation is undertaken outdoors and the operator wears a respirator for protection against organic vapors.

The monomer recovery process is completely closed, and there is little potential for leaks. In addition, employees are rarely in the area and, since it is located outdoors, exposure associated with this part of the process would be minimal.

Only one employee is needed per shift to operate both the reactor and recovery areas. The control panel is located in a closed, positive pressure room with a separate air system. It is estimated that the operator spends up to 50% of the shift in this room.

There are no local exhaust systems in this process area, and the general ventilation rate was not determined.

Fifty-four personal samples have been collected and analyzed so that employee exposure to butadiene, benzene and styrene can be determined.

- Butadiene - Only 6 of the 54 samples revealed a detectable level of butadiene. The maximum concentration was 8.9 ppm.
- Benzene - Only 9 of the 54 samples had detectable levels of benzene. These ranged from 0.07 ppm to a maximum of 1.99 ppm.
- Styrene - Of the 54 samples with detectable concentrations of styrene, the exposure levels ranged from 0.02 ppm to a high of 10 ppm for an average of 2.25 ppm.

All of the 54 personal samples reveal an exposure below the current permissible exposure limit for butadiene, benzene and styrene. These results demonstrate the high level of vapor containment achieved in the reactor and recovery areas.

Maintenance employees may also be exposed to process toxicants, particularly when working on equipment in the reactor and recovery area. Fifty-three samplers have been worn by maintenance employees during shift work.

- Butadiene - Twelve of the 53 samples had detectable levels.  
Range: 0.11 ppm to 15.22 ppm; average 5.22 ppm.
- Benzene - Three of the 53 samples had detectable levels.  
Range: 0.11 ppm to 1.60 ppm; average 0.73 ppm.
- Styrene - Six of the 53 samples had detectable levels.  
Range: 0.1 ppm to 1.41 ppm; average 0.69 ppm.

Maintenance employees are obviously not receiving a significant exposure to any of these toxic vapors.

#### Pigment Preparation Area

In the pigment preparation area, one employee makes up all the additive solutions for the reactors and for the coagulation area. The ingredients are made up and added to solution tanks in a chemical kitchen area. The toxicity of, and employee exposure to, these chemicals have not been studied by plant personnel and could not be evaluated during the survey. The fate of these chemicals as they proceed through the process is also unknown and should be the subject of further study.

The kitchen area was well ventilated and it appeared that good housekeeping was emphasized. Attempts are made to receive dry materials in flake or large

particle form, rather than as a fine powder. Also, material container sizes are selected to correspond as much as possible with the weight requirements of the various batches. This minimizes the need for the operator to weigh out short weights (removal of part of the contents in the bag to obtain the desired weight) of dry materials, which is usually a very dusty operation. All of the solution tanks are open to the room and are not provided with local exhaust. Further study of the chemical and toxicological characteristics is needed to determine whether the open tanks are a source of potential employee exposure.

### Coagulation Area

All of these tanks and operations in the coagulation area are open to the workplace and there are no observable exposure controls. The coagulation area includes the latex blend tank, the pigment addition tank, the coagulation tanks, the shaker screen and the reslurry tank. One employee works in this area. There are two broad areas of potential exposure related to chemical toxicants: 1) residual styrene and butadiene in the latex, and 2) the various chemicals or "pigments" added to the latex. Residual styrene and butadiene are not problems because of the effectiveness of the latex stripping operation. Plant data show that no butadiene remains in the latex and less than .06% styrene by weight. The bulk of the residual styrene left in the latex will be released in the dryer (under high temperature) and not in the workplace from the open tanks. Personal samplers were worn by two operators in the coagulation area and analyzed for styrene and benzene (butadiene was not analyzed because of its high permissible exposure limit and because plant data show that it is not in the latex at this point). Sample results are: 0.03 ppm benzene and 0.07 ppm styrene for operator #1, and 0.09 ppm benzene and 0.73 ppm styrene for operator #2. These results are well below current permissible limits for these two toxicants and, thus, demonstrate the effectiveness of the latex stripping process.

Potential employee exposure to the numerous chemical additives is not known. If some of the chemicals are volatile, their vapors may enter the workplace and pose a potential exposure. This is another area where additional research is necessary.

### Dewatering, Drying and Baling Areas

The filter and hammermill are not sources of potential employee exposure. The dryer could drive off any volatile material along with the water, but since it is vented to the atmosphere there is little possibility of workplace contamination. This conclusion is demonstrated by the results of two personal samplers worn by the dryer/baler operators: 0.01 ppm benzene and 0.28 ppm styrene for operator #3; and, 0.02 ppm benzene and 0.26 ppm styrene for operator #4.

The largest potential exposure related to the dryer is the cleaning operation, which is required once every 10 weeks. Crumb rubber falls from the dryer apron and must be dislodged and scraped out periodically, either by using a long rod, or by entering the dryer and manually removing it. The various tasks necessary for the cleaning operation have been studied extensively by computer analysis so that safer and quicker methods can be developed so that

the frequency of the operation can be reduced. This has resulted in the development of a strictly enforced standard operating procedure. Before any cleaning is done, a safe work permit must be completed and signed off by the appropriate supervisor. Employees who enter the dryer must tape their clothes (to prevent skin contact), wear impervious gloves and a head covering, and use a dust respirator.

The major potential for exposure at the baling station is airborne talc dust. Exposure has been largely eliminated by the following measures:

- Dry talcing of rubber bales was discontinued (bales are now coated with a talc slurry)
- Applying talc inside of boxes and between bales was discontinued (plastic sheets are now used)
- A nonasbestos-form talc was selected for use

Talc is still used on floors and certain equipment to prevent sticking, but this is not a large source of airborne dust.

#### LEAK DETECTION, PREVENTION, AND EQUIPMENT

##### Leak Detection

For the past several years, a comprehensive personal and area sampling program has been in use, primarily for butadiene, styrene and benzene. The major purpose of this program is to periodically monitor employee exposure to these toxicants. However, the program results also assist in locating problem areas where additional controls or maintenance may be necessary.

There is no automatic monitoring system or periodic leak detection protocol to locate process leaks rapidly after they occur. It is up to the operators to alert the maintenance department to conditions (such as leaks in valves or pump seals) that could lead to excessive employee exposure.

A program was initiated to determine any potential problems associated with the numerous chemicals utilized in the process. Suppliers have been requested to supply safety data sheets for their products outlining potential hazards and recommended work practices and engineering controls. A detailed evaluation is being undertaken to assess risks to employee health from these chemicals and to institute protective measures and air sampling programs where necessary.

#### PERSONAL PROTECTION EQUIPMENT

The pigment area operators are supplied with a half-face, disposable dust respirator, but its use is not required. Workers who enter the crumb rubber dryer are required to wear a combination dust and organic vapor respirator, gloves and head covering. To prevent skin contact with dryer residue, workers' clothing must be taped at the end of the sleeve and trousers.

In work areas where ammonia can be released (generally the reactor cooling coil system), a half-face canister respirator for protection against ammonia

is required. Safety showers are provided.

For emergency situations, an adequate number of supplied-air respirators is available and employees are periodically trained in the proper use of this equipment.

#### PLANNED OR ONGOING IMPROVEMENTS

- A completely enclosed, pressurized lunchroom facility is being erected for employee use. The supply air for the system will have a particulate filter and a carbon adsorption bank.
- The control panel and operation station for the coagulation process will be enclosed and pressurized through a separate air system with a particulate filter and a carbon adsorption bank. It is believed that the operator will spend approximately 50% of his time in this safe exposure area.

#### CONTROL OF OTHER POTENTIAL HAZARDS

Noise Location	Average Noise Levels (dBA)	Source and Comments
Reactor Area	86 - 91	Reactor agitator motor and pumps. No controls noted.
Recovery Area	97 - 107	Recovery pumps and compressors. No controls noted.
Coagulation Operators Stand	87 - 92	Hammermill and dryer. No controls noted.
Coagulation Unit - Upper Level	93	Agitator motors. No controls noted.
Hammermill - Bottom Level	95	Hammermill. No controls noted.
Stacker - Bottom Level	87	Hammermill. No controls noted.

Employees are required to wear hearing protection, if they remain in the compressor room for over 1 hour during a shift. The reactor/recovery operator's exposure as measured using personal dosimeters range from 53% to 169% of the maximum permissible level.

Hearing protection is required, if an operator remains between the hammermills at ground level for over 6 hours during a shift. The new enclosed panel for the coagulator operator will reduce exposure considerably.

Maintenance employees' exposure to noise has been reduced by eliminating the use of steam cleaning for filter baskets to cleaning inside of a furnace.

## APPENDIX A.9. PHENOLIC RESIN PRODUCTION - CASE STUDY #9

### PROCESS SUMMARY

The Novolak process for making phenolic resin is depicted in Figure A.9-1. It is a batch process and numerous phenolic resin products are manufactured using a variety of raw materials. Periodically, resorcinol will be used in the process instead of phenol.

Phenol is pumped from the storage tank into a closed weigh tank. When the proper weight is achieved, the phenol is dumped by gravity into a kettle. A separate, closed weigh tank is used to measure the other input materials including formaldehyde and xylene. This weigh tank is also located above the kettle and drops its contents by gravity at the appropriate time. Next, an organic acid catalyst is pulled into the kettle under vacuum through a closed piping system. A gas-fired heater raises the temperature of the reacting mass to 100°-200°C. The reaction takes from 18 to 40 hours depending on the batch formulation. The kettle is equipped with both a reflux condenser and water cooling coils which control the kettle temperature of the reacting mass.

After the completion of the reaction, the resin is dehydrated under vacuum at a temperature of 200°-260°C to remove water, and unreacted phenol and formaldehyde. The resin is then dropped onto a cooling belt where it is cooled and solidified, then fed to a flaker. The flaked resin is packaged and sold, or ground and cured with hexamethylenetetramine.

### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

#### Phenol

8 hour TWA - 5 ppm (19 mg/m<sup>3</sup>)

#### Formaldehyde

8 hour TWA - 3 ppm

Ceiling limit - 5 ppm

Peak level - 10 ppm for less than 30 minutes

### CONTROL TECHNIQUES

#### Monomer Feed System and Weigh Tanks

Both the phenol and formaldehyde feed pumps are located either in a tank room or outdoors and are not normally a source of employee exposure. Each weigh tank is closed and vented to the atmosphere. Unless there is vapor re-entry into the building from the weigh tank vents, this part of the process constitutes little hazard.

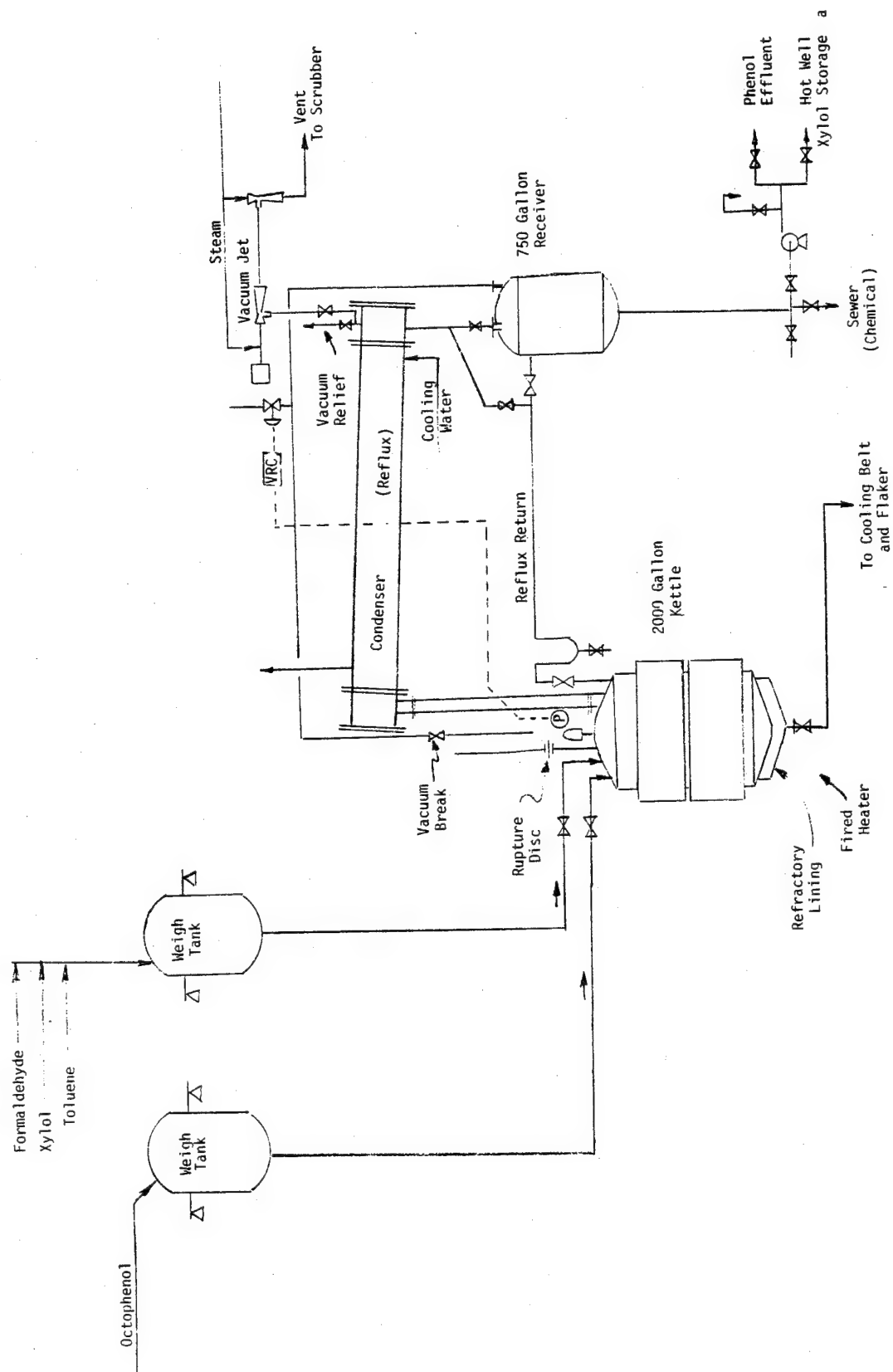


Figure A.9-1. Novolak Process for Phenolic Resins

## Kettle System

The weigh tanks are elevated relative to the kettles and the kettles are located above the cooling belt to permit material transfer through the process by means of gravity. Therefore, there are no pumps in the process building and a large potential source of workplace contamination is eliminated.

Each kettle is equipped with a fully automatic heating and cooling system that is controlled by instruments at the control panel. A recording temperature controller (TRC) reads out both the batch and jacket temperature. A heating-cooling switch is used in conjunction with the TRC to open either the steam or water line to the jacket. Because the batch temperature is closely controlled by this system, there is little potential for upset conditions or leaks due to overheating and thus pressurization of the kettle and condenser. All units are further protected by specified rupture discs.

The kettles are normally kept closed throughout the loading/unloading and reaction cycle. For certain resins, however, the manway must be opened to allow the operator to drop in small quantities of minor ingredients. The pressure in the kettle during the reaction is atmospheric (the rupture discs are set at 40 psi), which reduces the potential for leaks. During the dehydration cycle, the kettle is under vacuum and there is no potential for leaks.

## Reflux Condenser System

The reflux condenser system is depicted in Figure A.9-1. During full reflux, the condensate is returned directly to the kettle. At other times, it is collected in a completely enclosed azeo receiver and either pumped to the solvent recovery network or incinerated, depending on the percentage of free phenol and formaldehyde. In either case, the system is closed to the workplace and is not a source of vapor release.

The cold end of the condenser is connected to a vacuum system composed of two steam jet ejectors in series. The vacuum pulled on the kettle through the condenser is controlled by a recording vacuum controller mounted on a panel board. The steam ejectors either discharge directly outside the building or discharge to a vent scrubber.

It is extremely important that the procedure for applying and releasing vacuum be followed carefully to prevent "slugging" resin up into the condenser. From the time the ejectors are turned on until the prescribed vacuum is obtained, the operator must be present to control the rate of boiling in the kettle. Therefore, the light and sight glass must be clean to allow the operator to see the boiling in the kettle. If proper operating procedures are followed to control the boiling rate and prevent fouling the system, there should not be any significant leaks of vapor into the workplace.

## Kettle Cleaning Procedure

The kettles must be cleaned periodically. A caustic solution is used to remove residual resin. The solution is pumped into the kettle and heat is applied to assist in breaking up caked resin. The caustic solution is flushed out of the kettle along with any residue removed by the caustic. A



neutralization wash is then used to remove residual caustic. Next, the top and bottom manways are opened, the steam jet vacuum is started, and the kettle is swept for some time with clean air. Before the employees are allowed to enter for manual cleaning, the oxygen level is measured, all piping inlets are blanked off and the fuses are pulled from the kettle, from the agitator and from the kettle firing system. Also, an employee is stationed at the manway at all times when workers are in the kettle. The kettle cleaners must wear safety harnesses so that they may be pulled out quickly in case of an emergency.

### Reaction Chemistry Changes

A significant reduction in exposure downstream of the kettle has been achieved by modifying the reaction chemistry to reduce the percentage of unreacted phenol and formaldehyde in the resin. In addition to this, several types of scavengers are added to the batch to tie up unreacted phenol and formaldehyde following the polymerization cycles. It is reported that the percentage of unreacted phenol in the resin has been reduced to 1% and unreacted formaldehyde to 0.25%.

### LEAK DETECTION AND PREVENTION

#### Leak Detection

No procedure has yet been implemented to detect leaks from process equipment or to periodically measure employee exposure to phenol or formaldehyde.

### LOCAL EXHAUST VENTILATION SYSTEM

#### Kettles

The steam jet ejector system connected to the kettles is used to control vapor escape from the kettle when the manway is opened to add batch ingredients or when employees enter the kettle for manual cleaning. The velocity of the air flowing into the open manway with the vacuum system on is in excess of 0.762 m/s (150 fpm).

#### Cooling Belt

Two large canopy hoods are positioned over the feed end of the belt and draw approximately 0.040 m<sup>3</sup>/s (85 cfm) per square foot of the belt area. This airflow induces an inward velocity around the perimeter of the canopies of 0.508 to 1.524 m/s (100 to 300 fpm). The hoods appear to be effective. However, the exhaust for the section of the belt where the molten resin is dropped onto is not satisfactory due to insufficient airflow and poor closure.

### GENERAL VENTILATION

A series of wall- and roof-mounted propeller-type fans provide approximately 20 room changes per hour in the reactor area. This airflow can be increased to 60 room changes per hour in emergency situations.

## EXPOSURE DATA AND CONCLUSIONS

Area samples were collected for phenol and formaldehyde using charcoal tubes and gas detector tubes respectively. Eight 15-minute charcoal tube samples were collected for phenol in the general area around the kettles (3 of these were taken at the operator's desk). Each of these samples showed phenol concentrations below 1 ppm. Three detector tube samples for formaldehyde were taken in the kettle area at random times during a shift. Formaldehyde was not detected by any of the detector tubes. These data show that, under normal operating conditions, employee exposure to phenol and formaldehyde is negligible.

Six 15-minute charcoal tube samples for phenol were taken around the cooling belt. Three of the samples were taken adjacent to the hot roll just downstream of the second canopy hood (<1 ppm, <1 ppm, 2 ppm). Two detector tube samples for formaldehyde taken at the same location failed to detect any concentrations of formaldehyde. These samples show that the canopy hood exhausts are effective in removing unreacted monomer vapors from the workplace. The effectiveness of the hood is directly related to the speed of the belt which determines the retention time of the resin under the hood. The phenol sample result of 2 ppm was caused by cross drafts blowing across the belt. Two 15-minute charcoal tube samples for phenol and a detector tube sample for formaldehyde were taken directly adjacent to the dump area where the molten resin is dropped onto the belt. The measured concentrations of phenol (5.2 ppm, 6.4 ppm) are relatively high and indicate the need for better enclosure and exhaust for this exposure source. The detector tube sample did not detect any formaldehyde and this reflects the effectiveness of the reaction chemistry changes implemented to reduce unreacted monomer.

A one-hour charcoal tube sample for phenol was collected at the bagging station, where the operator for the entire area spends most of his time. The measured phenol concentration was less than 1 ppm. This sample shows that the area operator is not excessively exposed to phenol or formaldehyde although a significant amount of vapor is escaping at the hot end of the cooling belt.

At the end of the cooling belt, the dry resin sheets are dumped in a flaker, which breaks up the resin for feeding to the bagging station. Both the bagging station and the flaker are potential dust sources. Two consecutive total dust samples collected in the bagger/flaker operator's breathing zone yielded an average exposure concentration of 2 mg/m<sup>3</sup>. This is well below the OSHA standard of 15 mg/m<sup>3</sup> for total nuisance dust.

## APPENDIX A.10. ALKYL PHENOL RESIN PRODUCTION - CASE STUDY NO. 10

### PROCESS SUMMARY

The process is designed for the batch production of a large variety of alkyl phenol resin products with wide variations in raw materials, operating temperatures and reaction times. Figure A.10-1 presents a schematic of the basic process steps for a typical alkyl phenol resin.

Xylene, caustic and butyl phenol are first batched into a mixing tank. The xylene is metered directly into the tank and the butyl phenol and caustic are gravity fed from an elevated weigh tank. Bags of other raw materials and other minor ingredients are dumped into the mixing tank through an open manway. After the manway has been closed and sealed, formaldehyde is added to the vessel at a controlled rate from an elevated weigh tank. The batch is held at the reaction temperature for several hours or until the desired degree of reaction is attained. At this point, hydrochloric acid is piped into the tank to neutralize the reaction.

Through several water washings, the batch is phase separated into xylol-resin layer and a water and xylene layer. The waste water is pumped or drained (depending on the density of the resin solution relative to water) into a closed sewer system and pumped to the water treatment system. The resin is pumped to an elevated holding tank.

From the holding tank, the resin is dumped into one of three kettles. Under heat and vacuum, the remaining water and xylene are vaporized, condensed and recovered. The dehydrated resin is then dumped into a large cooling pan, where it is cooled and solidified. The resin is broken up into chunks, loaded in barrels and conveyed to the crushing area. In the crushing area, the resin lumps are ground and packaged in bags.

### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

Of primary concern are formaldehyde, alkyl phenols and xylene, all of which are used in large quantities.

#### Formaldehyde

8-hour TWA - 3 ppm  
Ceiling limit - 5 ppm  
Peak level - 10 ppm for less than 30 minutes

#### Alkyl Phenols

8-hour TWA - 5 ppm (19 mg/m<sup>3</sup>)

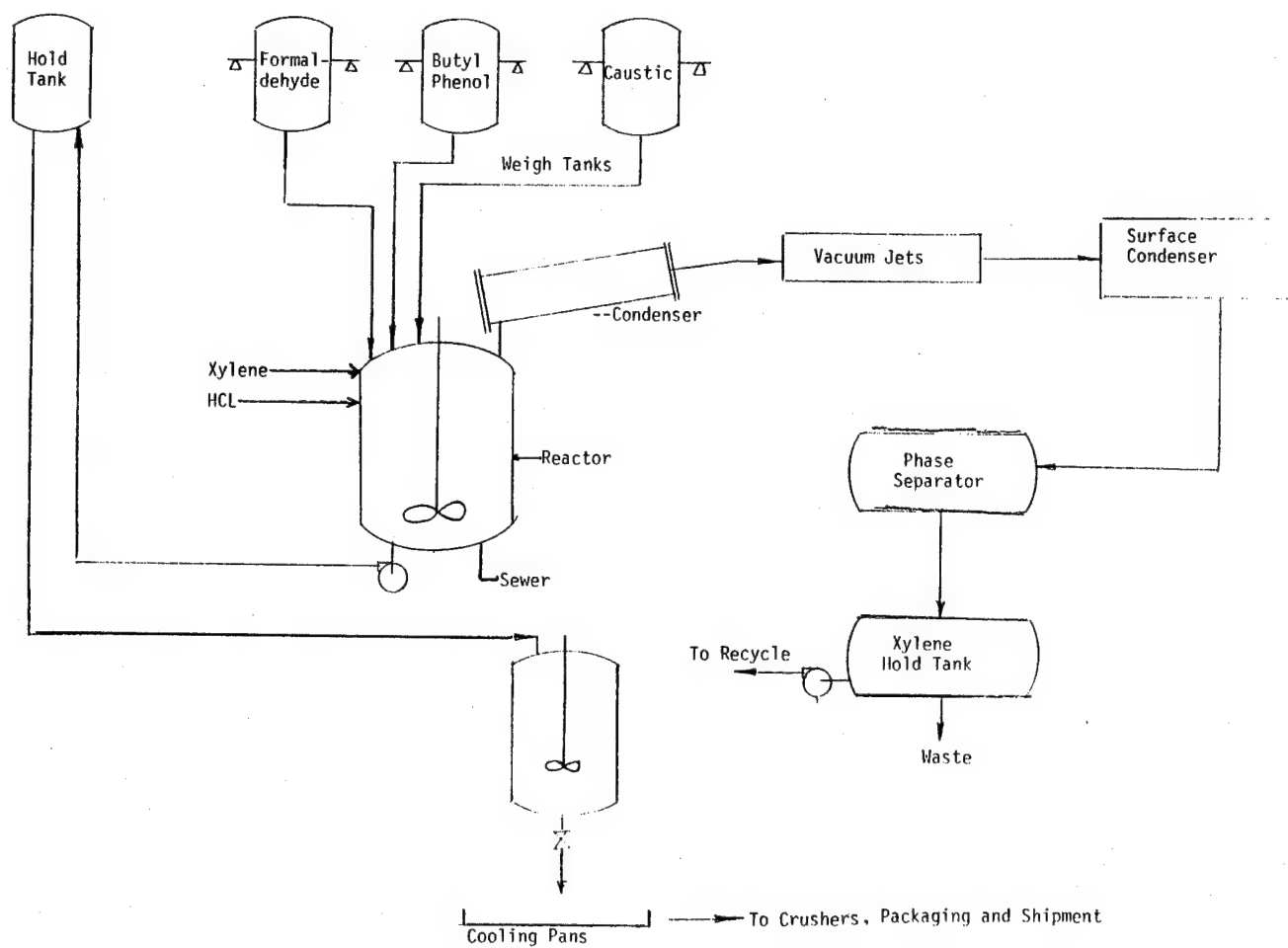


Figure A.10-1. Alkyl Phenol Resin Process

## Xylene

8-hour TWA - 100 ppm

### Minor Additives

There are numerous minor additives used in the various resin products manufactured at this plant. Many of these are acids and caustics.

### CONTROL TECHNIQUES

#### Process Design, Modification and Maintenance

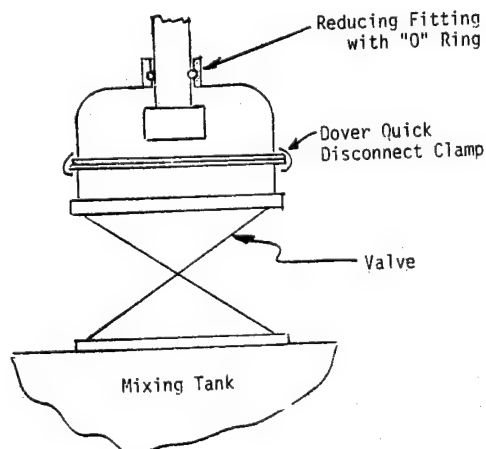
##### Vessel Cleaning--

Vessels are now cleaned automatically, so employees do not have to enter and risk exposure either by contact or inhalation. This is now possible because of the following.

Product scheduling-- Modification in scheduling among different batches enables continuous operation for about one week without vessel cleaning. To illustrate how this scheduling is accomplished, suppose there are three categories of resin: A, B and C. Resin A cannot tolerate certain ingredients in Resin C, and vice versa. However, Resin B is not sensitive to ingredients in either Resin A or Resin C. Therefore, Resin B is scheduled for production in between runs of the other two resins. It acts as a buffer, segregating sensitive resins without the necessity of potentially hazardous and time consuming cleaning operations.

Caustic or solvent cleaning-- Depending on the resin produced, either xylene or a dilute caustic solution is used to clean the vessels. Each is pumped into the vessel and under conditions of heat, agitation and reflux, residual resin is removed. The xylene is recovered for future use. The caustic wash is neutralized with a hydrochloric acid wash and transferred to the water treatment system. A neutralization wash follows any caustic wash. All of this is accomplished with the vessel closed and vapor escape is minimal.

Sample collections-- Before a batch is transferred from the mixing tank to the holding tank, a sample must be collected and pH tested. Rather than open the manway to collect the sample, the operators use a homemade sampling port.



Although this method does not eliminate vapor escape, it greatly reduces it. Operators claim to be able to collect a sample and close the valve in less than 20 seconds.

Weigh tanks-- Each weigh tank is equipped with a high level alarm gauge. This eliminates the possibility of catastrophic releases of phenol or formaldehyde due to overloading the tank.

Because the tank is on scales, the vent and feed lines are not attached or in contact with the tank. There are small annular spaces between each line and the tank through which vapors can escape into the workplace, particularly during the charging operations. However, weigh tanks do have exhaust blowers to evacuate the area where the lines enter the weigh tanks.

Sewer trunk system-- Several years ago, the sewer system was rebuilt and completely sealed. Contaminated process or cleaning liquids are now piped to the closed sewer for transfer to the new water treatment system. This has eliminated a significant potential for airborne or contact exposure with various toxicants.

Batch recipe changes-- Plant engineers have made slight batch recipe changes to attempt to reduce the amounts of free, unreacted phenol and formaldehyde in the resin following the distillation operation. In essence, these changes allow the reaction to closely approach 100% completion, with little or no unreacted monomer. This has the mutual benefit of reducing employee exposure by contact and inhalation, as well as lowering the potential of dermatitis among customer workers' handling of product.

In addition to recipe changes, small amounts of chemical scavengers are added to the kettle following the reaction sequence. These additives inhibit the activity of the residual butyl phenol and render it waste water treatable.

#### Sinker Resins

Some resins, due to their molecular weight characteristics, tend to sink to the bottom of the mixing tank during the phase separation operation. This condition requires the operator to pump off the water phase from the top of the tank, rather than simply drain it to the sewer through the bottom of the tank. This is more time consuming and it increases the possibility of vapor escape because the manway must be open during the operation. Plant engineers are having some success in reducing the frequency of sinker resins by adding more xylene to the batch. This reduces the density of the xylene/resin mixture and allows it to float to the top of the tank. Thus, the water can be drained from the tank without opening of the manway.

#### Vessel Design Modifications and Maintenance

Failures periodically occurred around certain critical points on the vessels due to stress corrosion. Following investigation, this was found to be caused by an accumulation of salts and carbonates normally found in the process water. These salts were deposited at critical joints because certain flanges and connections anchored to the vessel had dead zones from which water would not drain. As the water evaporated, salts and carbonates

accumulated on the metal surfaces and caused granular corrosion during vessel heat up. This situation has been successfully avoided by modifying flanges and connections to eliminate all dead spaces. Further, the joints and connections were smoothed to reduce the number of points where corrosive materials could accumulate. When the plant is shut down for two weeks during every summer, all seams are inspected for corrosion and all weld joints are rebuilt, if required.

Heat exchanger surface failure also occurred periodically. Studies found that the corrosion was caused when the Dowtherm fluid was improperly transferred through the heat transfer areas. The operators would thermally shock the whole reactor vessel by introducing Dowtherm at 315°C (600°F) into the reactor which was at room temperature. These shocks produced cracked welds. A rigidly enforced standard operating procedure resolved this problem and the resulting potential for employee exposure. The procedure requires the operator to heat the reactor at a much slower rate.

## WORK PRACTICES

### Vessel Entry Procedure

Before any employee enters a process vessel (weigh tank, mixing tank, reaction kettle) for any reason, a Confined Space Preparation and Entry Authorization must be completed by the area supervisor. This is critically important due to the severe consequences of skin contamination with phenol. The plant has a well established rule that any employee entering a vessel without first following the vessel entry procedure will be immediately terminated with no exceptions.

## LEAK DETECTION AND PREVENTION

### Leak Detection

There are no automatic monitoring systems to alert operators to high concentrations of toxicants or for the location of leaks. Gas detector tubes and portable hydrocarbon detectors are periodically used to monitor certain process areas for excessive concentrations of toxic gases and vapors. Operators and supervisors watch for leaks in process equipment and report these to maintenance. It is reported that frequent checks of all leak-prone equipment are performed by supervisory personnel.

## LOCAL EXHAUST VENTILATION

### Mixing Tank Vent Scrubber System

At certain times during the process, the mixing tank manways must be opened. To prevent vapor escape into the workplace when the tanks are open, the mixing tank vent scrubber system (refer to Figure A.10-2) induces a negative pressure on the vessel.

The system was apparently designed to produce an inward flow of .508 m/s (100 fpm) through the open manways of the mixing tanks. However, during the survey (with only one manway open) the system was only able to produce an

airflow of .152 to .254 m/s (30 to 50 fpm). Observation indicated that vapors were surpassing this control and contaminating the workplace. It was judged that the low flows were due to corrosion in the mixing tank vent scrubber system.

The exhaust header arrangement on the mixing tank is such that the system also pulls a slight vacuum on the cold end of the condenser.

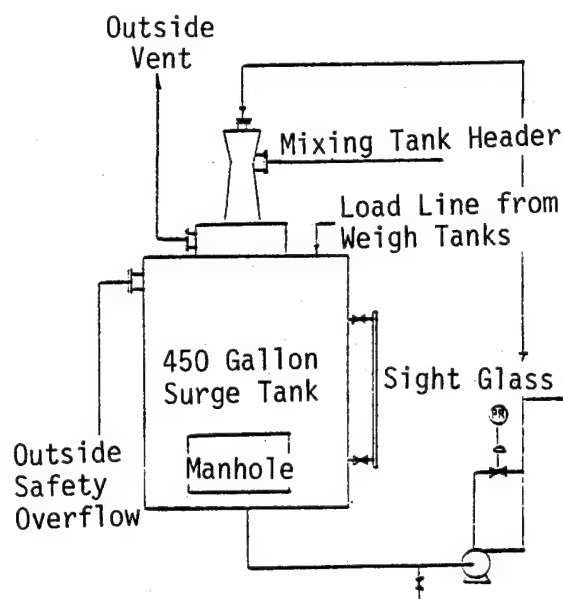


Figure A.10-2. Mixing Tank Vent Scrubber System

### Reaction Kettle

Mixing tanks where reactions take place are all tied into venturi vent systems. During the dehydration process the kettles are under vacuum and any leaks would thus be into rather than out of the vessels.

### Cooling Pans

There are two potential hazards associated with the use of the cooling pans: 1) when the resin is first dropped from the kettles, unreacted phenol and formaldehyde vapors may be given off before the resin has cooled, and 2) when the solidified resin is broken up, a significant amount of dust is generated (posing both an inhalation and dermatitis problem).

At the rear of each cooling pan, there is an exhaust pulling approximately 8000 cfm as measured during the survey. However, adjacent cooling pans are not partitioned and cross-drafts across the pans destroy much of the containment potential of these exhausts. Further, employees are using pedestal fans to increase cooling. This practice contributes to the relative ineffectiveness of the exhaust system. If the individual cooling pans were segregated with partitions and lower ceilings were provided, it is likely that the exhausts would be effective.



## GENERAL VENTILATION SYSTEM

There are numerous propeller-type general ventilation fans in the process building. These were installed some time ago and there are no prints from which to determine air turnover rates. Particularly during winter, it is doubtful that much air is moved through the building by this system.

## DRAWING BOARD CONTROLS

Several future controls are being planned or considered:

### Xylene Extraction

Xylene condensed from the distillation kettle is phase separated, reclaimed and recycled back into the process. Consideration is being given to using this xylene to extract the resin from the wash waters dropped into the sewer. The xylene, containing trace amounts of these ingredients, would then be used as feed stock for the subsequent new batch of phenolic resin. This extraction stage would reduce the load on the waste water treatment plant and recover products.

### Metering System

Presently all solutions are added to the appropriate vessel through a metering system; other materials are pumped in through weigh tanks or by other means. Plans to install metering systems for alkyl phenols, formaldehyde and hydrochloric acid are being contemplated. This should eliminate the need for weigh tanks and the resulting potential for worker exposure. In the case of hydrochloric acid, it may preclude the necessity of collecting samples to check resin pH.

### Belt Flaker

Batch formulas are being examined to determine if changes can be made to permit the resin to be transferred directly to a belt flaker. This would greatly reduce the use of the cooling pans. Obviously, this change would eliminate a large source of dust and dermal exposure.

Certain resins would continue to be dumped into the cooling pans for solidification. One of the present hazards is related to opening of the kettle spout to dump the resin. Currently an operator must unbolt a hinged manway and then signal to the kettle operator to relieve the vacuum on the vessel. As the pressure is equalized, the weight of the resin pushes the manway open and allows the resin to drain into the pan. Occasionally, the manway sticks and there is a considerable danger of workers being splattered with resin at temperatures up to 176°C (350°F). A pneumatically operated assembly is being designed and will be evaluated on a test reactor. The system will remove the last bolt and pneumatically pry the manway open. The Flager Company has details of this system upon request.

#### ADDITIONAL CONTROL TECHNIQUES CONSIDERED

- Resin facilities would be designed for complete air changes every 3 minutes (20 air changes/hour).
- Standby emergency blowers would be available to provide an air change every minute (60 air changes/hour) in case of a solvent spill.
- Control rooms would be provided for operators to monitor the entire process. Air-operated valves would allow the operators to spend most of their time in the control room.
- Pitched floors would be provided in all areas to permit total washing of the floors for good housekeeping purposes.
- All weigh tanks would be totally enclosed to prevent emission of vapors.
- High pressure water (10,000 psi) blaster, manufactured by Haliburton Systems, would be used for washing floors and equipment to remove accumulated resins.
- Batch distillation would be eliminated and replaced by continuous solvent removal.

#### EXPOSURE DATA AND CONCLUSIONS

Plant personnel are just beginning a rigorous air sampling program so no data on employee exposure to alkyl phenol, formaldehyde or xylene were available. Personal and area samples were collected for xylene and area samples were collected for alkyl phenol and formaldehyde to estimate employee exposure. These data are summarized in Table A.10-1.

Employee exposures to xylene, alkyl phenol and total dust are clearly well below their respective recommended limits. Workplace concentrations of formaldehyde are equal to or slightly less than the recommended exposure limit of 3 ppm. The concentrations are well above the NIOSH recommendation of 1 ppm formaldehyde for any 30-minute period. Since the exhausts for the mixing tanks were not functioning properly (.152 to .254 m/s [30 to 50 fpm] through open manway), a detector tube sample was collected for formaldehyde just above an open manway. The concentration was measured at greater than 40 ppm. This is undoubtedly the major source of employee exposure in the area, and it is felt that workplace formaldehyde levels would be substantially reduced if the exhausts were functioning properly. It is also interesting to note that the formaldehyde concentration is about equal throughout the process building, even in areas remote from exposure sources. This reinforces the belief that the general ventilation was not moving much air in this building.

The personal sample results for employee exposure to total dust while removing resin from the cooling pans are well below the permissible exposure limit of 15 mg/m<sup>3</sup>. These results are surprising as there were very noticeable clouds of resin dust being generated. However, the employees were positioning themselves such that the combined action of the pedestal fans and the rear exhaust was directing the dust away from (rather than through) their breathing zones.

Area Samples (collected with colorimetric indicator tubes)				
Location	Xylene (100 ppm)	S A M P L E R E S U L T		
		Formaldehyde (3 ppm)	Phenol (5 ppm)	
Operator Breathing Zone (OBZ) - between weigh tanks	15	3	<1	
OBZ - between mixing tanks	17	3	<1	
OBZ - between kettles	10	2	<1	
OBZ - kettle operator's deak	15	2	<1	
OBZ - at cooling pan after resin dropped	ND	1	<1	
OBZ - at cooling pan, resin being broken up	ND	1.5	<1	

Personal Samples				
Employee	Toxicant	Sample Time	Sample Result	OSHA TWA Exposure Limit
Kettle Operator	Xylene	10:38 am - 11:43 am	5.5 ppm	100 ppm
Kettle Operator	Xylene	2:25 pm - 3:40 pm	3.5 ppm	100 ppm
Kettle Operator Helper	Xylene	10:40 am - 12:00 n	2.7 ppm	100 ppm
Kettle Operator Helper	Xylene	12:06 pm - 2:00 pm	4.7 ppm	100 ppm
Kettle Operator Helper	Xylene	2:05 pm - 3:35 pm	3.7 ppm	100 ppm
Employee Breaking Up Resin in Cooling Pan	Total Dust	2:05 pm - 2:35 pm	<0.8 mg/m <sup>3</sup>	15 mg/m <sup>3</sup>
Employee Shoveling Resin Out of Cooling Pan	Total Dust	2:08 pm - 2:38 pm	2.0 mg/m <sup>3</sup>	15 mg/m <sup>3</sup>

Table A.10-1. Air Sample Data

## PERSONAL PROTECTIVE EQUIPMENT

Scott air packs are readily available for use during an emergency situation such as a spill or line rupture. Employees are trained and retrained in the proper use of this equipment. Otherwise, employees may, at their option, wear chemical cartridge respirators for protection against organic vapors. The use of these respirators is usually limited to periods when an operator senses nasal irritation to formaldehyde.

Whenever a process vessel must be entered or a line containing phenol or formaldehyde is opened, employees must wear a full rubber suit (including gloves, head covering and boots), a face shield and respiratory protective devices. Other than for these tasks, no particular protective clothing is provided. Employees exposed to resin dust at the cooling pans are asked, but not required, to wear long-sleeved shirts to reduce the risk of skin contact. Respirators for protection against airborne particulate are provided, but not required.

## CONTROLS OF OTHER POTENTIAL HAZARDS

### Noise

Noise levels in the process area range from 82 dBA to 85 dBA around the weigh tanks, mixing tanks and kettles. Through conversations with plant engineers and observations made during the study, it was determined that no noise abatement modifications have been made. Because the noise levels are below the permissible limit of 90 dBA, no hearing protection is required. The noise levels in the cooling pan area average 87 dBA to 90 dBA. The major source of this noise is the blowers for the rear exhausts on the cooling pans. As before, no noise abatement modifications were noted or observed.

## APPENDIX A.11. LIQUID AND SOLID EPOXY PROCESS - CASE STUDY NO. 11

### INTRODUCTION

This case study involves an epoxy resin manufacturing facility that has been shut down while undergoing a major modernization and expansion. The study consisted primarily of a review of general specifications for new equipment to be used in unit operations in older plants where exposure of workers to hazardous chemical agents is known to occur. These general specifications were prepared by plant engineers and hygienists familiar with the occupational health problems associated with epoxy manufacture.

### SUMMARY OF LIQUID AND SOLID EPOXY RESIN PROCESS

A generalized block diagram of the processes is presented in Figure A.11-1. In the liquid resin process, an excess of epichlorohydrin is reacted with bisphenol A to form an intermediate chlorohydrin compound. The sodium hydroxide reacts with the chlorohydrin to form epoxy linkages on diglycidyl ether of bisphenol A. The excess chlorohydrin is removed and reaction is continued further after the addition of a ketone solvent and more sodium hydroxide. The solution of the resin in the ketone solvent is washed with water to remove residual salt; the water is decanted and discarded, and the solvent is removed by vaporization and recycled.

In the solid resin process, no excess of epichlorohydrin is used during the reaction between epichlorohydrin bisphenol A and sodium hydroxide. The ketone solvent is added to dissolve the resin and the mixture is washed to remove the salt by-products. The water is then decanted and processed to an effluent treatment system and then discarded to waste. Ketone is removed by vaporization and recycled. The molten resin is drained, cooled and then crushed and ground to a fine solid.

### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

Diglycidyl Ether of Bisphenol A

TWA - 0.5 ppm

Epichlorohydrin

TWA - 5 ppm

### CONTROL TECHNIQUES

Pressurized Double Mechanical Seals

The liquid resin reactors are equipped with double mechanical seals with high pressure steam condensate maintained between the seals to insure that no

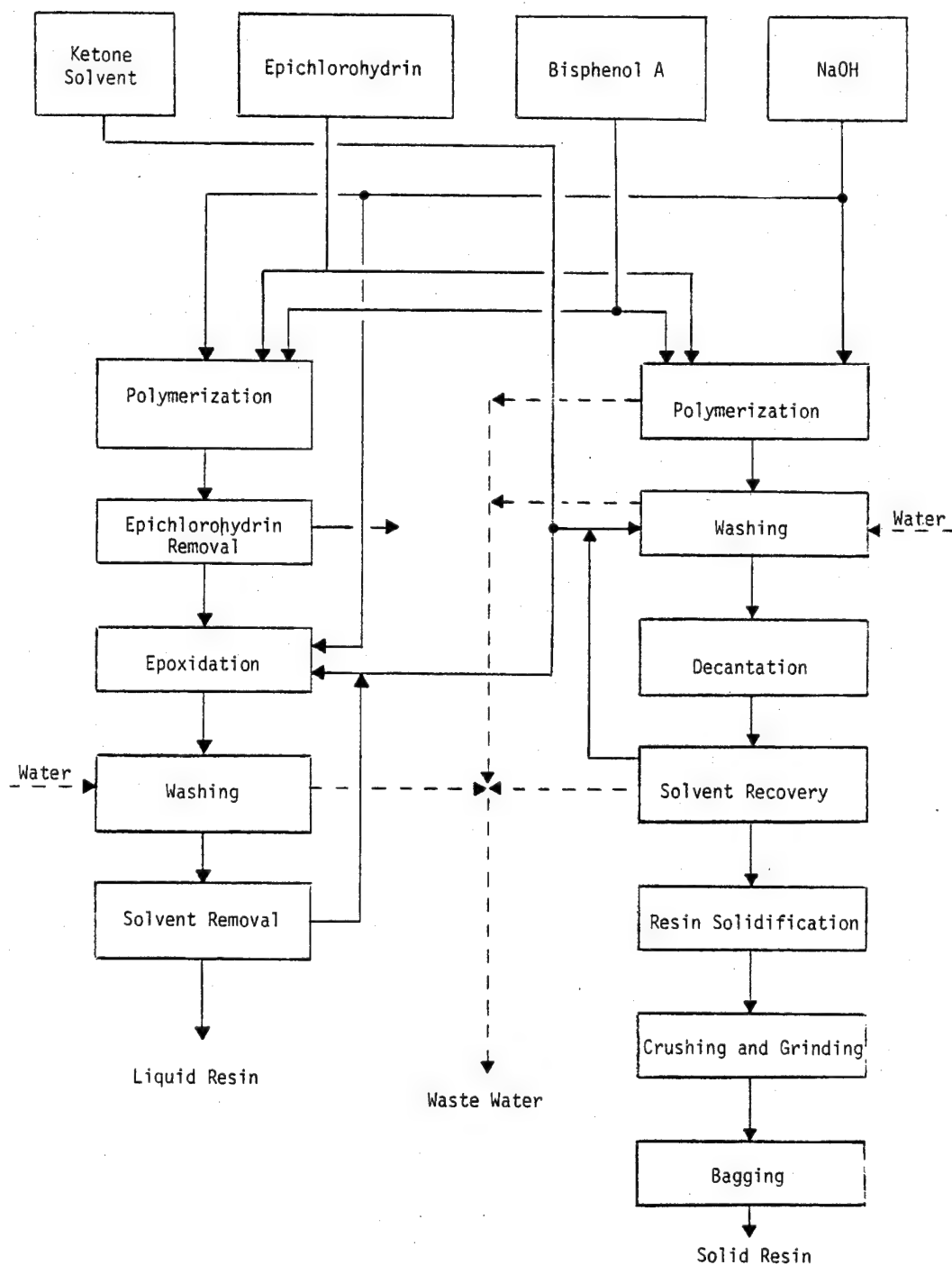


Figure A.11-1. Liquid and Solid Epoxy Resin Processes

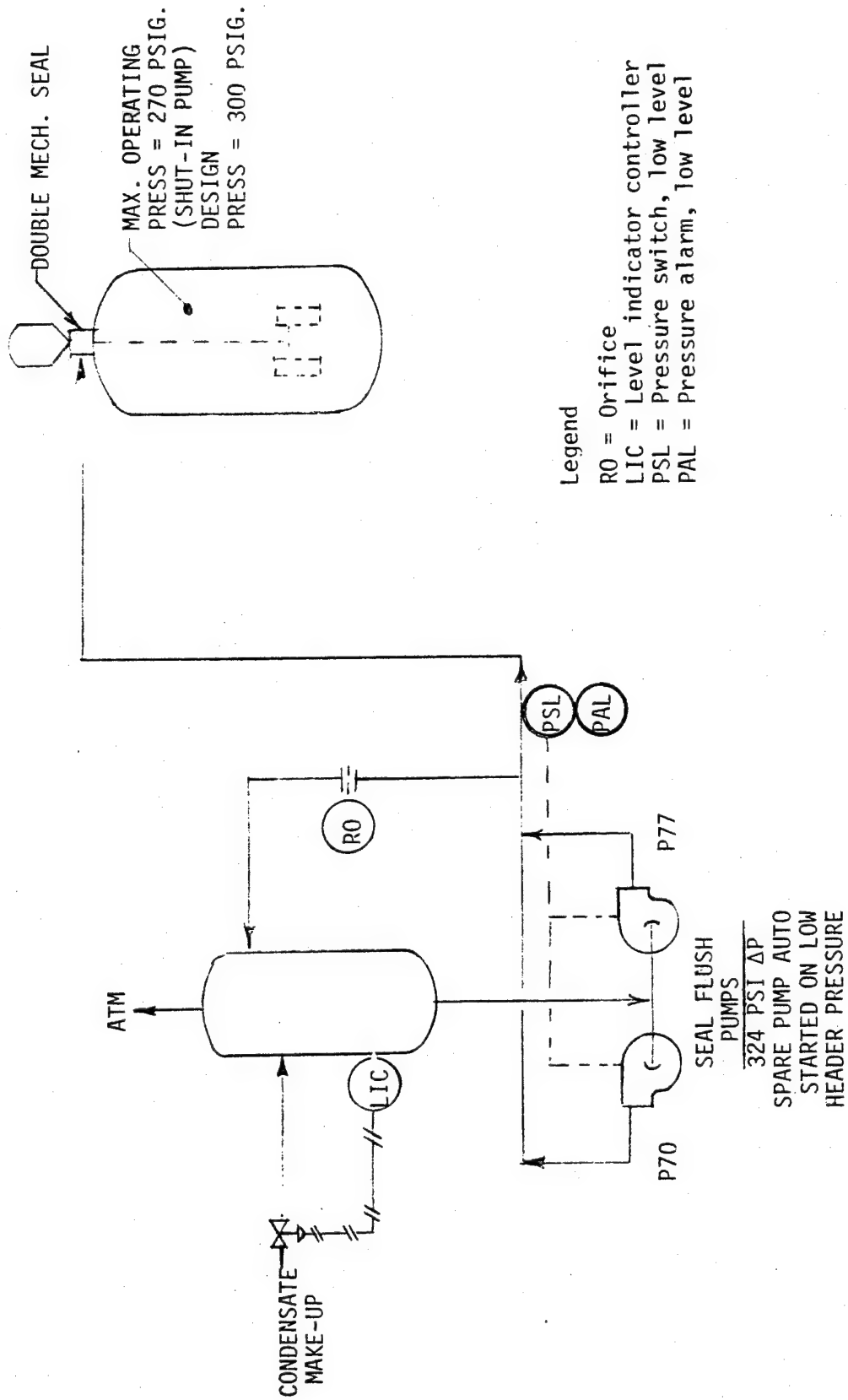
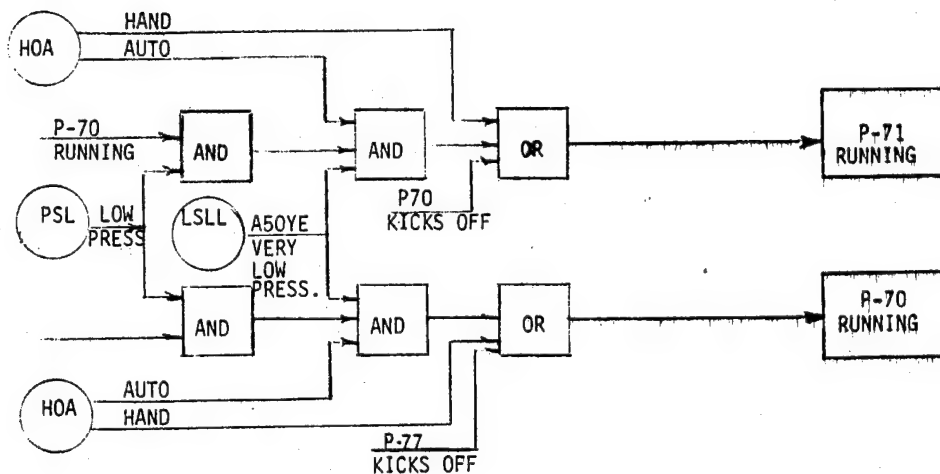


Figure A.11-2. Fail-Safe Pumping System



AND	A logic gate that gives a positive electrical signal when all inputs are positive
OR	A logic gate that gives a positive electrical signal when any one or more of the inputs is positive
HOA	Manual override
PSL	Pressure switch - low pressure signal gives a positive signal to AND gate
LSLL	Level switch - low level gives a null signal to AND gate

Figure A.11-3. Specifications for Control Interlock System



material leaks from the reactor to the work environment. In the event of a seal failure, steam condensate would leak either into the reactor or the work environment, depending on the failure mode. Steam condensate pressure is maintained on the agitator seals by means of a fail-safe pumping system described in Figure A.11-2. The general specifications for the control interlock system and how the standby pump is activated are given in Figure A.11-3.

#### Pump Splash Guards

All rotating equipment shafts in liquid resin service where toxic liquid is being handled are equipped with sheet metal splash guards and the splash zone encased by the guards is hard piped to the drain collection system. General specifications for splash covers for two types of pumps are listed in Figures A.11-4 and A.11-5.

#### Splash Covers

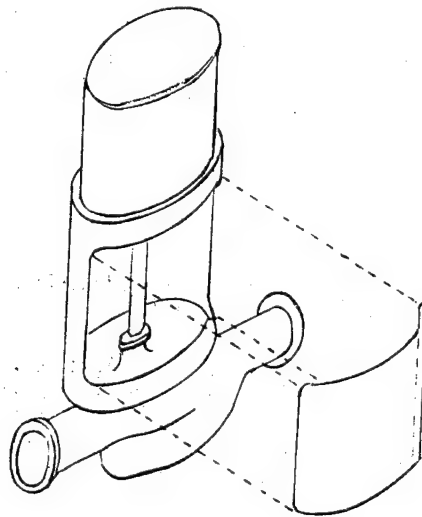


Figure A.11-4. Splash Cover for Vertical In-Line Pump - General Specification

- (1) Splash covers shall be furnished in place of coupling guards when so specified on pump data sheets.
- (2) In the event of catastrophic seal failure, covers shall divert lost fluid to a 1.90-cm (3/4-inch) drain connection in the casting.
- (3) Covers shall be drip-tight and gasketed with resilient material resistant to pumped fluid. Enclosed area shall be vented to atmosphere.
- (4) Attaching hardware shall be stainless steel.
- (5) Covers shall be attached to pump nozzle with stainless steel chains

to prevent loss of covers when removed for maintenance.

- (6) Outside piping connections to stuffing box area shall be run through the casting using bulkhead fittings.

SPLASH COVERS

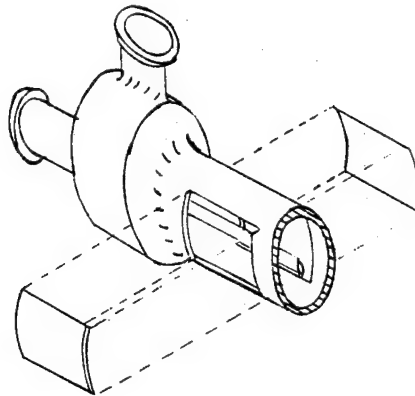


Figure A.11-5. Splash Cover for Refinery Type Centrifugal Pump-General Specification

- (1) Splash covers shall be furnished on refinery type pumps when so specified on the pump data sheets.
- (2) In the event of catastrophic seal failures, covers shall divert lost fluid to a 1.90-cm (3/4-inch) drain connection in the bottom of the bearing bracket casting.
- (3) Covers shall be drip tight and gasketed with resilient material resistant to pumped fluid. Enclosed area shall be vented to atmosphere.
- (4) Attaching hardware shall be stainless steel.
- (5) Covers shall be attached to pump baseplate or pump frame with stainless steel chains to prevent loss of covers when removed for maintenance.
- (6) Outside piping connections to stuffing box area shall be run through bearing bracket casting using bulkhead fittings.

#### Process Equipment Drains

Process equipment used with liquid resins must be drained and steam cleaned prior to entry or maintenance by workers. Hard piping the drain and steam lines and providing a sight flow glass in the drain line makes the draining and steam cleaning of equipment convenient for the maintenance personnel. Combining work procedures requiring signing of inspection and entry forms by two personnel before opening the equipment eliminates the risks of accidental exposure. Figure A.11-6 illustrates a typical hard pipe drain installation for process equipment containing hazardous material.

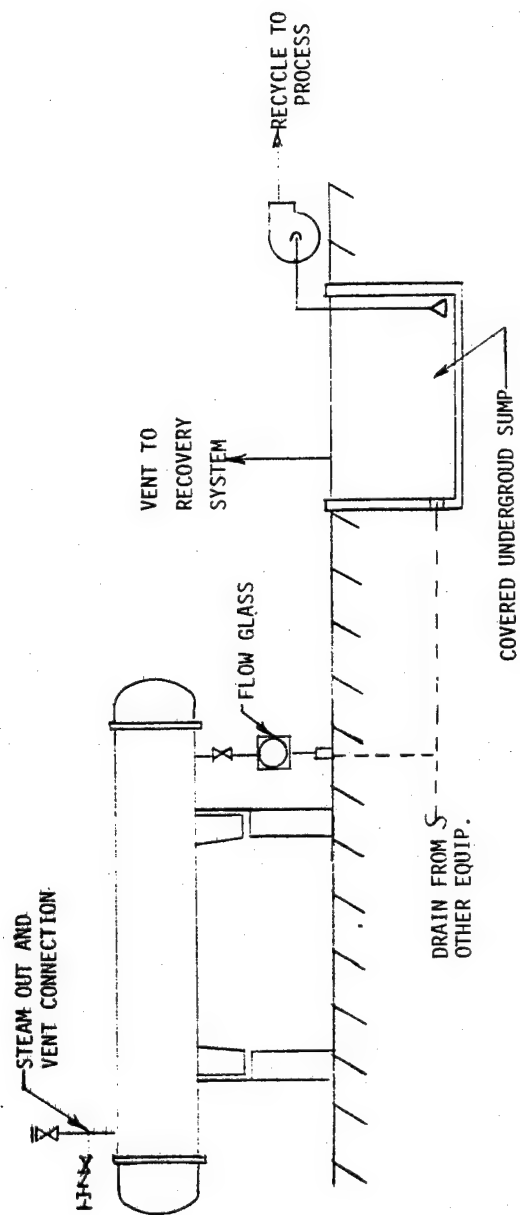


Figure A.11-6. Typical Hardpiped Drain for Process Equipment Containing Hazardous Material

## Bag Filters

Bag filters in liquid resin systems that require opening to replace bags are equipped with an automatic decontamination system to block in, drain out, steam out and water wash the bag filter and the filter enclosure prior to opening. An operational logic description of the filter backwash system is given in Figure A.11-7 and a process and instrument flow diagram of the "Off-Spec" recycle filter is shown in Figure A.11-8.

## Emergency Pressure Relief in Case of Fire

In the event of fire, process equipment in liquid resin service is designed to discharge the vessel contents when high pressures are reached. The overflow is sent to a collection header to remove hazardous materials from the personnel work area.

## Instrumentation of Resin Processes and Shipping Facilities

The solid and liquid resin processes and shipping facilities are instrumented for control by Programmable Logic Controllers (PLC's), which are set up to provide constant surveillance of the process - piping lineups, process variables, process excursions, etc.

## Solid Catalyst Unloading and Charge System

Exposure of workers to solid catalysts during normal plant operations is eliminated by the Catalyst Vacuum Loader described in Figure A.11-9. The solid catalyst for the solid resin facilities is unloaded from drums into a charge system via a vacuum conveying system to eliminate contact with personnel and generation of dust. The sensors and control elements interface with a computer and are automatically controlled. The system is packaged by Vac-U-Maz Company.

## Transfer of Hot Molten Resin

In order to eliminate any need for maintenance of equipment such as pump seals during transfer of molten resin, the reaction kettles are elevated above the solidification facilities to permit gravity flow through rigid piping.

## Truck and Tank Car Loading Arms

Filling of tank truck and tank cars with liquid resin and/or resin solutions is via vapor loading arms when connected to the truck or car hatches. Two liquid level probes (capacitance-type probes mounted in loading nozzle assembly) automatically cut off filling at predetermined levels. Closed collection systems catch pump drips and sample purges for respective process units. Vapors are collected and removed from operating personnel areas. Specifications for a tank car loading arm system are given in Figure A.11-10.

## Drumming Area

Hoods are provided to remove vapors from the work area. Resin drippings are collected and returned to the process.

OFF-SPEC RECYCLE FILTER RF-1 DECONTAMINATION SYSTEM. This system involves the decontamination procedure which precedes the replacement of filter bags. This filter has only one shell and a filter bag. Consequently, off-spec recycle shall cease for the time the decontamination procedure is carried out.

RF-1 decontamination system and associated instrumentation are shown on flow sheet in Figure A.11-8. Filter RF-1 and the other two bag filters RF-2 and RF-3 can be decontaminated simultaneously if necessary. The differential pressure across the Off-Spec Recycle Filter, RF-1, is sensed by PDT-1. When this differential pressure increases to 15 psi, the contacts of PDSH-1 will open sounding alarm PDAH-1. This signal does *NOT* go to the programmable controller. Therefore, decontamination of this filter is not automatically initiated. When PDAH-1 sounds, the operator will be required to go to the field and initiate the decontamination sequence.

The operating mode of the filter is determined by HS-1, which is a three-position switch labeled "run", "safe", and "wash." When HS-1 is switched from the "run" position to the "wash" position, this signals the programmable controller to control the decontamination sequence.

Upon receiving a signal from HS-1, the programmable controller will control the decontamination cycle according to the following sequence:

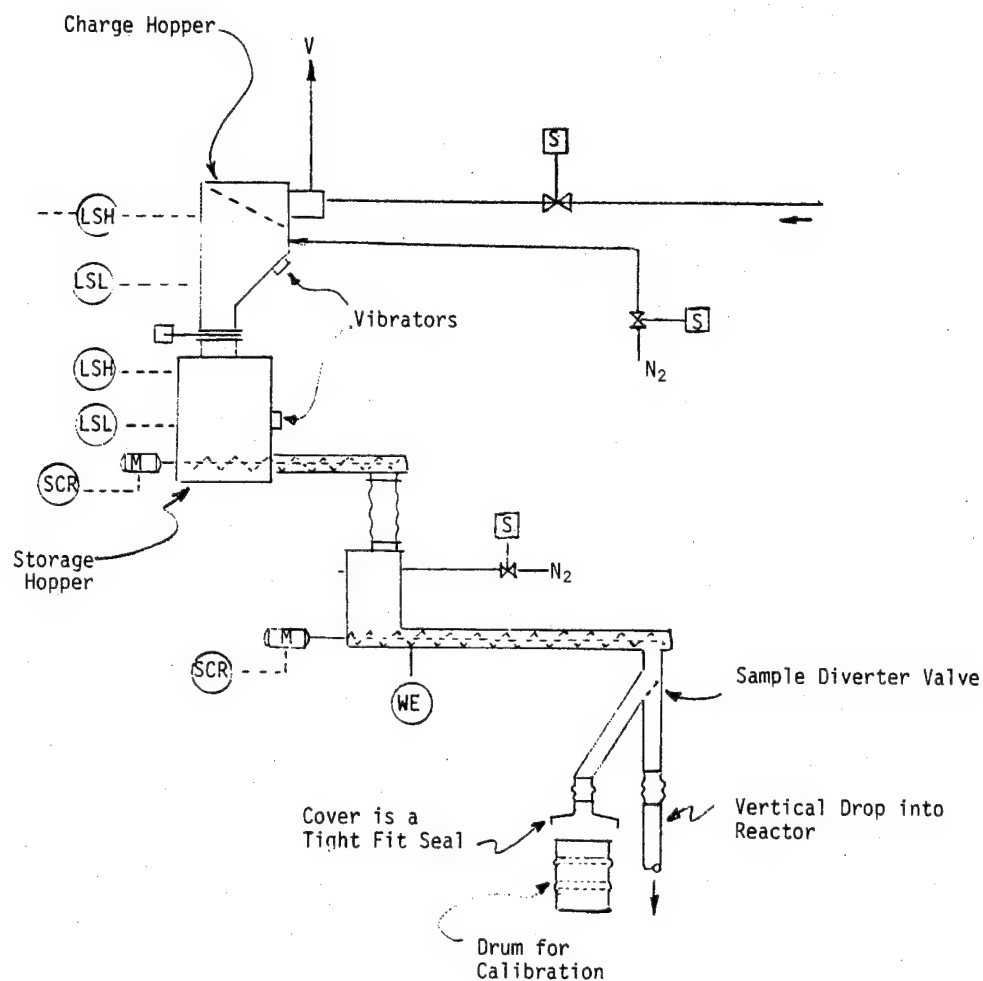
1. Status light ST-1 on the panel board will come on steady.
2. The programmable controller will energize solenoid valves V-10 and V-22 causing the feed and filtrate valves V-10 and V-22 to close. This will cause the feed pump to recirculate back to the feed tank via its flow orifice.
3. When the feed and filtrate valves have been confirmed closed by their respective limit switches, solenoid valve V-20 will energize, causing blow-down valve V-21 to open. This will allow material from the filter shell to be blown back to the feed tank.
4. When the blow-down valve has been confirmed open by its limit switch, solenoid valve V-13 will be energized causing steam valve V-12 to open. This will admit steam to the filter shell. When the steam valve has been confirmed open by its limit switch, a timer in the programmable controller will start which will hold this valve open for 15 seconds, adjustable to 30 seconds. When this blow-down time period has expired, solenoid valves V-13 and V-20 will deenergize, causing the steam and blow-down valves V-12 and V-21 to close.

Figure A.11-7. Filter Backwash System

Figure A.11-7. (continued)

5. When the steam and blow-down valves V-12 and V-21 have been confirmed closed by their respective limit switches, solenoid valve V-22 will energize causing the aqueous sewer valve V-19 to open.
6. When the aqueous sewer valve V-19 has been confirmed open by its limit switch, solenoid valve V-17 will energize causing the water valve V-18 to open. This will permit water to flush through the filter shell to the aqueous sewer. When the water valve has been confirmed open by its limit switch, a timer in the programmable controller will start which will hold this valve open for 15 seconds, adjustable to 30 seconds. When the water wash time period has expired, solenoid valve V-17 will deenergize causing water valve V-18 to close. The aqueous sewer valve V-19 will remain open.
7. When the water valve V-18 has been confirmed closed by its limit switch, solenoid valve V-15 will energize causing vent valve V-14 to open. When the vent valve has been confirmed open by its limit switch, status light ST-1 on the panel board and status light ST-2 in the field will flash to indicate that the sequence is complete and that the filter bags are ready to be replaced.
8. Before opening the filter to replace the bags, the operator will turn HS-1 to the "safe" position to deenergize solenoid valve V-24. This will block and vent the instrument air header supplying all automatic valves on this filter and thereby return all valves to the closed position.
9. After changing the filter bags and closing the filter shell, the operator will switch HS-1 to the "run" position. This will energize solenoid valves V-10 and V-16, causing the feed and filtrate valves V-11 and V-22 to open at a controlled rate. The two status lights ST-1 and ST-2 will go out.





Legend:

- (LSH) Level Sensor, High
- (LSL) Level Sensor, Low
- (SCR) Motor Control
- (M) Motor
- (WE) Weight Sensor
- X-S Valve, Electrically Activated

Figure A.11-9. Catalyst Vacuum Loader



TRUCK AND TANK CAR LOADING ARMS

1. SCOPE This specification covers the minimum requirements for the design and fabrication of loading arm assemblies used in loading of fluids into trucks and tank cars at the company's plant.
2. PIPING CODE The fluid carrying parts shall be designed and fabricated in accordance with ANSI B31.3 and the latest addenda.
3. OSHA All equipment furnished shall meet the requirements of Part 1910, Subparts G and H, Occupational Safety and Health Standards, of Title 29, Code of Federal Regulations.
4. DESCRIPTION The items numbers, type, design details, and fluid data for each assembly are specified in the data sheets covering the specific installation.
5. MATERIALS The materials of construction for the metallic part and elastomer seals and gaskets that are in contact with the fluid shall be selected for maximum compatibility. Materials in contact with the fluid must not contain copper or zinc in any amount. Pipe shall be Schedule 40 seamless ASTM A53-B carbon steel. Flanges to which the load arms will be connected are 150-pound, raised face, Schedule 40 carbon steel, ASTM A-105, 4-inch size for the fluid line and 3-inch for the vapor line. Valves are required in the arm lines at the outermost end. The fluid line valve shall be a Jamesbury ANSI Class 150 flanged ductile iron ball valve, catalog number AZ150-F21 or equivalent. The vapor line valve shall be a 150-pound, ductile iron butterfly, Demco Series NE or equivalent.
6. BEARINGS The bearings in the swivel joints shall be conservatively designed for long life and low friction for ease of movement. They shall be easily replaceable.
7. SEALS Provide seals to prevent fluid from contacting the bearings. Seals shall be readily replaceable without dismantling the end connections.
8. LUBRICATION Provide grease fittings for lubricating the bearings. These shall be located in a readily accessible area.
9. COUNTERBALANCING Provide spring counterbalancing units or a mechanical assist that will permit the unit to be easily lowered to the loading position and stay down automatically or by means of a locking device. They shall be compact and not inhibit the rotation freedoms within the design limits.

Figure A.11-10. Truck and Tank Car Loading Arms

Figure A.11-10 (continued)

10. VAPOR RECOVERY The loading will be done through hatchways 18-inches, 20-inches and 24-inches nominal diameter. The loading arm shall be designed to provide full vapor recovery with fluid lines arranged for free draining. Provide an adapter plate that will form a tight closure for the range of sizes indicated. The plate shall be an integral part of the loading arm.
11. LEVEL SENSORS A two-level sensing device is required. The probe depth shall be adjustable and the relative depths of the two probes shall be adjustable from 1- to 3-inch differential. The probe system to be furnished to the field is a Capacitive Level Probe as manufactured by Drexelbrook. The probes with protective shields may be mounted in the adapter plate. Provide a 3-inch gauge hatch for dip stick check of fluid level.

### Resin Dust Collection

A centralized vacuum cleaning system is provided to collect and remove resin dust from the worker environment. Both bag filters and wet scrubbers are used to separate the resin from the air sucked in by the vacuum system.

### Liquid Resin Filters

Liquid resin filters are designed to minimize employee exposure by the use of regenerable, wire-wound elements with automated back-wash system. The automatic filter system (Reactogard II) is manufactured and marketed by Ronninger-Petter. The filter system cycle adjusts automatically to variations in the solid content of the feedstock.

## APPENDIX A.12. TOLUENE DIISOCYANATE PROCESS - CASE STUDY NO. 12

### PROCESS SUMMARY

The toluene diisocyanate (TDI) unit is a typical petrochemical plant, located entirely out-of-doors with enclosed processes. The TDI production facility occupies part of a large complex. Immediately adjacent to the TDI unit are the toluene diamine and phosgene production facilities which provide the input materials for TDI synthesis. The operators control the process from a control room about 50 yards away.

As shown in Figure A.12-1, the major steps in this process are reaction, fractionation (phosgene and hydrochloric acid separation, solvent recovery and TDI distillation) and TDI transfer to storage.

The phosgene and toluene diamine are dissolved in a solvent, monochlorobenzene, and mixed in a series of reactors where additional phosgene is added. The temperature of the reacting mass increases from ambient temperatures in the first reactor to about 200°C in the last reactor. The reacted mass is transferred to a series of fractionation columns where the unreacted materials, by-products and the solvent are separated from the TDI. In the first fractionating column, the excess phosgene and the hydrochloric acid by-product are removed. The phosgene is recovered and recycled. The TDI product is separated from the heavy components in the third fractionating column. Additional fractionation of the heavy components produces some crude TDI which is recycled to the solvent recovery column.

The purified TDI product is transferred to drum and tank car storage. The residue is cooled in sheds prior to burial. Fumes released by the residue in the shed are exhausted into an incinerator.

### TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

#### Phosgene

Federal regulations require that employee exposure to phosgene shall not exceed an 8-hour time-weighted average of 0.10 ppm. This operation was designed with a high degree of control in mind.

#### TDI

The current standard for TDI specifies a maximum permissible airborne exposure ceiling limit of 0.02 parts per million of air. Some TDI is released to the ambient air during removing and cooling of the residue, sampling of product stream and pumping. Transient leaks occur at the flanged connections, especially during ambient temperature changes.

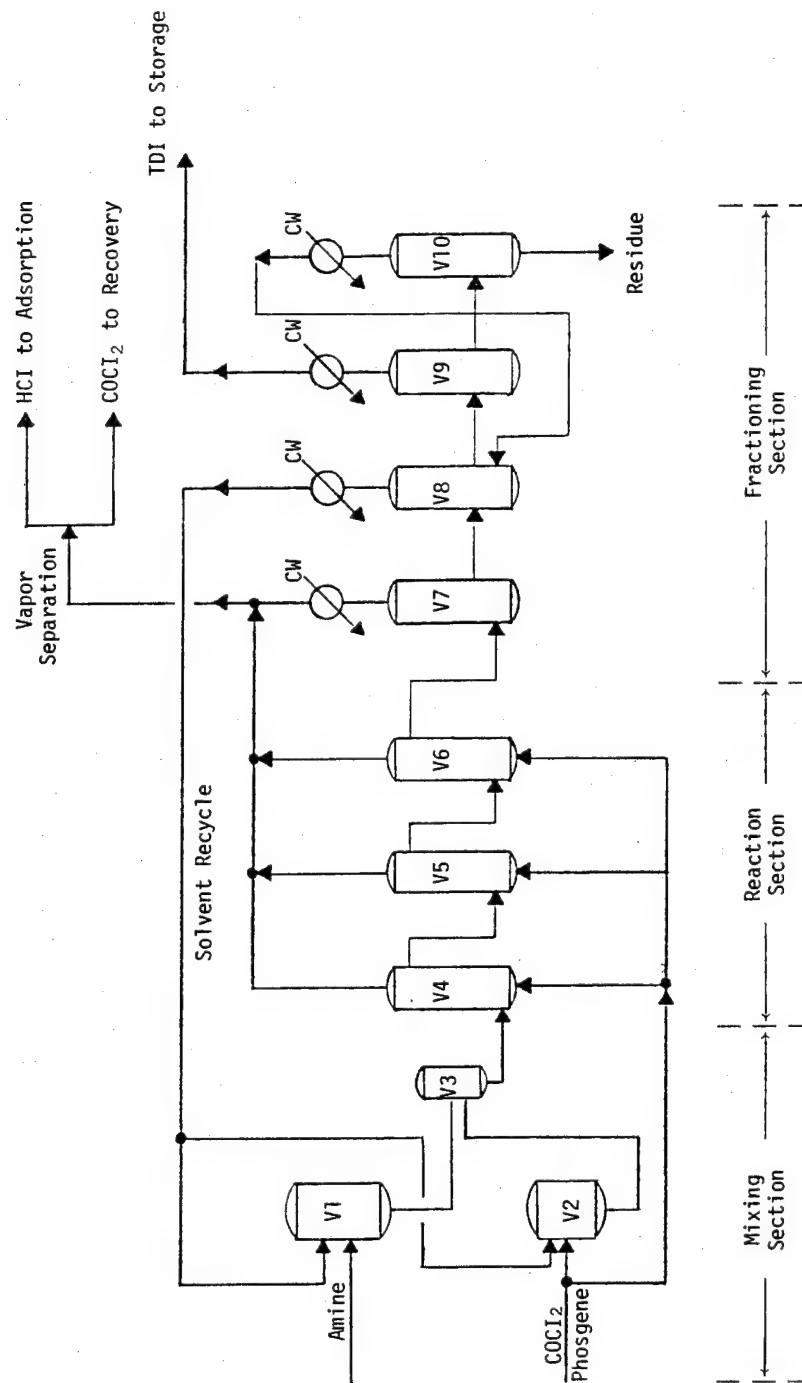


Figure A.12-1. TDI Process Flow Sheet

## Monochlorobenzene

Federal regulations require that employee exposure to monochlorobenzene is not to exceed an 8-hour time-weighted average of 75 ppm. Some monochlorobenzene is released to the ambient air during material transfer by pumping.

## Hydrogen Chloride

The ceiling value of 5 ppm in the breathing air was adopted by the American Conference of Governmental Industrial Hygienists.

The current permissible exposure limit for HCl is 5 ppm (7 mg/m<sup>3</sup>).

## Sodium Hydroxide

Sodium hydroxide is used as an aqueous solution and exerts no vapor pressure. Mists containing sodium hydroxide may be generated when the caustic scrubber is not operating properly. Federal regulations require that employee exposure to sodium hydroxide shall not exceed an 8-hour time-weighted average of 2 mg/m<sup>3</sup>.

## CONTROL OF TOXIC CHEMICAL AGENTS

### Process Design, Modification and Maintenance

#### Inherent Operating Characteristics--

The unit processes prior to the residue removal step are totally enclosed and a relatively high degree of exposure control is attained. Also, closed loop control is used to maintain the desired operating conditions in the process. Analog process controllers are installed on panels in a control room located about 45.7 m (150 feet) from the process area. There is no need for operators to be in the process area, except for routine inspection, sampling of process streams and emergency maintenance.

The residue removal and disposal steps and subsequent TDI transfer and loading operations are not automated and require considerable operator interaction.

#### Residue Removal--

The residue from the distillation unit is removed at frequent intervals and conveyed to a residue shed. Since the residue contains TDI, some TDI vapor escapes into the ambient atmosphere during this operation. While in the shed the residue will continue to release TDI vapor - for this reason, the shed is kept under a negative pressure and the exhausted air is incinerated to destroy TDI vapors. Ultimately, the residue is transferred by trucks to a burial area. All persons concerned with residue removal and disposal are equipped with respiratory protective equipment.

#### Maintenance--

There are two types of maintenance: emergency and turnaround. For emergency maintenance, every attempt is made to do on-stream repairs while the plant is operating in order to avoid hazards and production losses associated with equipment shutdown. Only a major breakdown would result in plant shutdown.

There are certain maintenance operations which would result in release of TDI if the plant is in operation, thus increasing the ambient air TDI concentration with high concentrations in the immediate area. During on-stream maintenance, it is essential that the maintenance workers be protected with air supplied respirators. Maintenance work is accomplished as quickly as possible both to restore normal operation and to minimize contamination of the plant environment. To further reduce worker exposures, a portable exhaust ventilation system is provided with various interchangeable hoods that can be placed over emission points to remove TDI. The exhaust of this system is discharged into the caustic scrubber. Turnaround maintenance is usually done once a year when the TDI production facility is completely closed down.

#### Drum and Tank Car Filling--

This operation usually occurs in an area of buildings some distance from the TDI production area so that the chance for cross-contamination is minimized. Hose nozzles are surrounded by exhaust hoods to remove TDI vapor; vapors from the system are removed in the scrubber. The TDI production plant is designed to meet the 0.02 ppm current ceiling standard. However, because of inherent problems in a manufacturing process, the ceiling standard is occasionally exceeded. These peaks are generally confined to the area of the plant where the temporary emission occurred. Workers are usually aware of high emission points and protect themselves from elevated concentration by the use of respirators.

### LEAK DETECTION AND PREVENTION

#### Description of Instruments

Area monitors for TDI (MDA, Model 7000) are of limited value because of the 15-minute lag in the response of the instrument to changes in TDI concentrations and difficulty in correlating worker location with instrument readings. These area monitors serve to help identify work areas that could result in worker exposure and which need immediate attention.

Personal TDI monitors (MDA miniature continuous TDI monitors) are worn by all persons working in the area. However, since air respirators are required to be worn by workers during maintenance in areas of potential exposure, the TDI monitor readings can be much higher than actual exposure experienced by the workers.

#### Sampling

Process samples are taken at frequent intervals during a production shift. An exhaust hood is located around the sample point. Unless proper care is used, there may be some spillage of TDI and release of vapor to the atmosphere. This amount of TDI would not significantly effect the overall concentration of TDI in the production area, although a momentary peak might be observed near the sampling site. The procedure, unless properly controlled, could result in a significant proportion of the daily TDI dose for the worker taking the sample.

During the sampling procedure, it is desirable for the sampler to wear an air supplied respirator to minimize the daily dose and to prevent a high exposure

for a short period.

#### Spills--

Despite the best efforts to prevent spills, these occasionally happen due to ruptured lines, leaking pumps or equipment, or for other reasons. When this happens, all personnel, except those assigned to cleanup duties, are required to evacuate the plant area. Personnel assigned to cleanup are equipped with protective clothing including gloves, splash goggles, overalls, boots and supplied air respirators. The TDI plant has a standard operating procedure that utilizes a water solution of ammonia and a wetting agent for neutralizing and cleaning up spills.

#### Important Equipment Features

##### Pump--

A major contamination source is leaking or malfunctioning TDI pumps. This problem can be minimized by several procedures. One is the use of oil pressurized double mechanical seals. If one seal fails, the second seal will prevent leakage for a period of time. A drop in oil pressure results from a seal failure and the pressure drop is visible by inspection of the oil reservoir at the pump. A second method of control is a gas evacuation system for each process pump. This consists of a hood connected to an exhaust system surrounding each pump.

#### General Ventilation

General ventilation is provided in the control room by means of a filtered air supply. The control room also contains the worker change room.

#### Ongoing Improvements

Elephant trunk hoods for pump venting of pumps and other equipment.

#### EXPOSURE DATA AND CONCLUSIONS

##### Toluene

The following TWA data were collected for the plant operators on three shifts carrying personal samplers (MDA Model 7000):

<u>Shift</u>	<u>TWA, ppm</u>
8:00 am to 4:00 pm	.011
4:00 pm to 11:00 pm	.007
11:00 pm to 8:00 am	.009

The difference between indicated concentrations was not statistically significant.

Typical exposure data for maintenance men recorded on personal monitors (MDA Model 7000) and wearing respirators during certain operations are given on the following page.



<u>Shift</u>	<u>Recorded TWA, ppm</u>
8:00 am to 4:00 pm	.011
4:00 pm to 11:00 pm	.015
11:00 pm to 8:00 am	.012

Peak concentrations from .03 ppm to .08 ppm were recorded on the personal monitor strip chart.

In the TDI loading area, a 54-hour personal sampler gave the following results:

<u>Reading, ppm</u>	<u>Cumulative Time</u>	<u>Frequency of Occurrence</u>
.009 TWA	Averaged TWA's	--
<.005	1145 minutes	--
.005 to .010	655 minutes	--
.01 to .02	325 minutes	21 peaks
>.02		10 peaks

At the residue outlet from the distillation unit where the operators wear respirators, an area monitor gave the following results:

<u>Reading, ppm</u>	<u>Reading % of Time</u>
<.005	72
.005 to .010	20
.01 to .02	11
>.02	7

#### PERSONAL PROTECTIVE EQUIPMENT

Employees are required to use supplied air line respirators when working on residue removal, TDI sample collection, cleaning up of spills and maintenance of equipment contaminated with TDI. Aqueous ammonia solutions containing wetting agents are used for cleaning up TDI spills.

## APPENDIX A.13. PHENOLIC RESIN COMPOUNDING PROCESS - CASE STUDY NO. 13

### PROCESS SUMMARY

The major process steps for this compounding plant are depicted in Figure A.13-1.

Solid phenolic resin in drums or pans is transported into the grinding room in the basement of the building. A forklift dumps the resin from these containers into a feed chute and the large lumps of resin are ground into .635-cm ( $\frac{1}{4}$ -inch) particles and are pneumatically conveyed to a roof-mounted collector.

From the collector, the ground resin is gravity fed into one of the two mixers (while one is mixing, the other is being charged). When the additives are thoroughly dispersed in the resin, the batch is pneumatically conveyed to another collector.

The resin and dispersed additives are ground into a fine powder. Each grinder discharges through a pneumatic conveyor to a separate collector.

Each collector dumps part of the batch in each of two ribbon mixers to standardize the resin particle size. Filler materials are then dumped into the mixers and dispersed in the resin.

The batch is next conveyed pneumatically to a collector and dumped into a mixer used as a holding tank. Resin is dropped at a controlled rate into one of two heated roll mills where heat and pressure fuse the resin and additive particles into a solid sheet material. The sheets are cut from the rolls, dropped into an enclosed trough conveyor, and fed into a hot breaker mill. The solid resin is ground into 2.54-cm (1-inch) chunks which are conveyed to another collector.

The collector feeds a screw conveyor which drops the resin into cutters. The cutters reduce the particle size further, and discharge through a screw conveyor into a pneumatic conveyor. The particles are collected and dumped into screeners. The screens separate the resin into oversize particles, fines, and the desired resin which is conveyed to outside hold tanks.

From the hold tanks, the resin is pneumatically conveyed to a blender which gives a uniform blend and smoothes off the particles. The blended resin is then pneumatically conveyed through a classifier into a hold tank.

The flow of resin from the hold tank can be manually diverted to a bag or drum packer for final packaging.

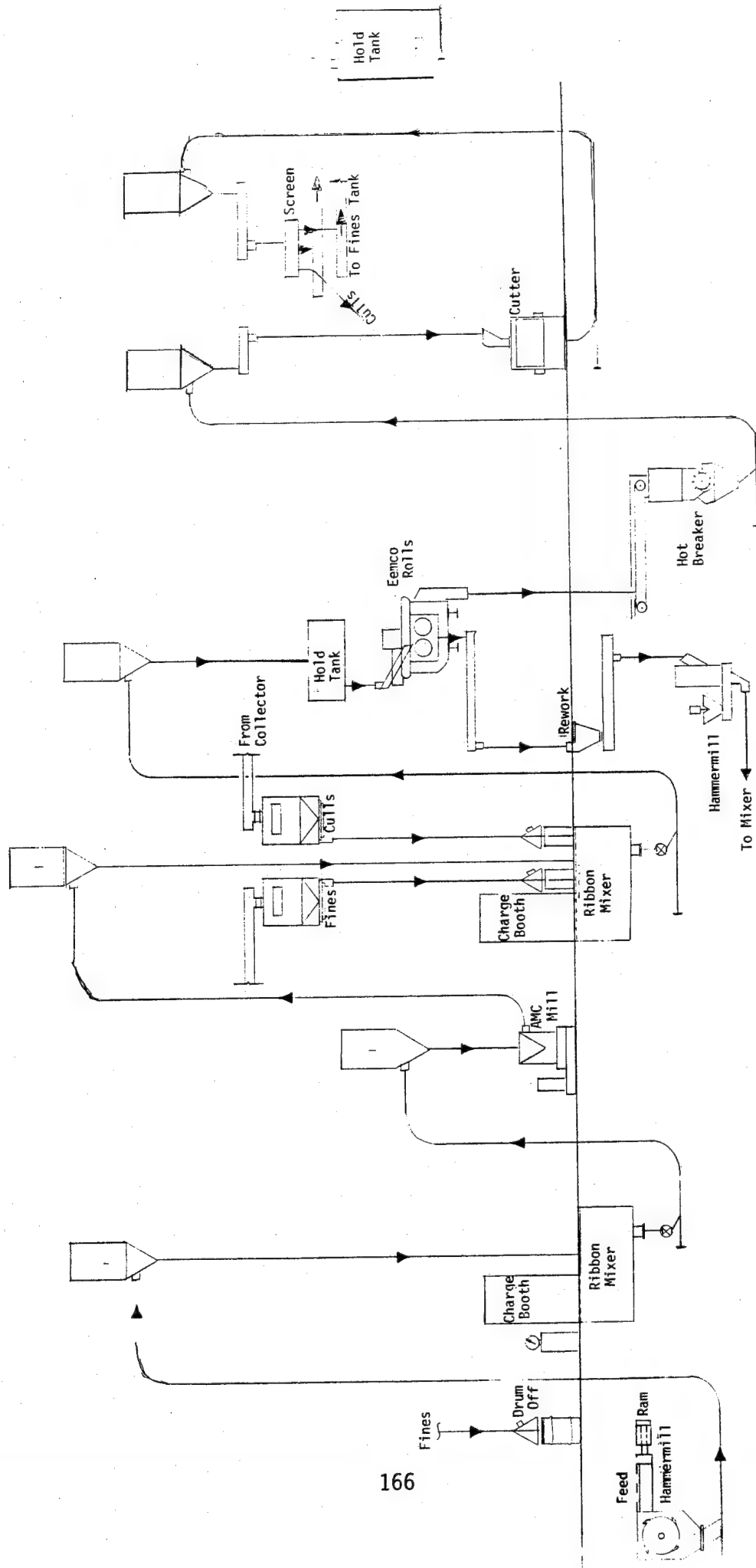


Figure A.13-1. Phenolic Resin Process Flow

## TOXIC CHEMICAL AGENTS AND HARMFUL PHYSICAL STRESSES

The potential for employee exposure to toxic chemical agents results from airborne dust in the workplace. Depending on the location of the source of emission relative to the process stream, the dust may consist solely of phenolic resin particles or a combination of the resin and various compounding ingredients.

For all process operations up to the first set of mixers, any dust escaping to the workplace air will contain only phenolic resin. This is considered a nuisance dust (TLV - 5 mg/m<sup>3</sup> respirable particulate), although it may contain very small amounts of unreacted formaldehyde and phenol. However, to lessen the potential for contact dermatitis, it is important to limit airborne concentrations to this level.

The most significant exposure potential occurs when the dry additives are dumped into the mixers. At the first set of mixers, the following ingredients are added:

- hexamethylenetetramine (no exposure limit, moderately toxic, skin irritant)
- diatomaceous earth (TLV - 1.5 mg/m<sup>3</sup> respirable particulate)
- glycerol monostearate (no TLV, nontoxic)
- lime (TLV - 5 mg/m<sup>3</sup> respirable particulate)

Additives used at the second set of mixers include:

- asbestos (TLV - 2 fiber/cc > 5  $\mu$  length)
- cotton flock (TLV - 1 mg/m<sup>3</sup>)
- carbon black (TLV - 3.5 mg/m<sup>3</sup>)
- coal dust (TLV - 2 mg/m<sup>3</sup>)
- nitrosine (no TLV)
- wood flour, paper flock (TLV - 5 mg/m<sup>3</sup> respirable particulate)

## EXPOSURE DATA AND CONCLUSIONS

This plant is operated continuously using a total of 24 employees. Prior to outlining the sampling data, it is helpful to describe job classifications.

- Bagger - Operates packout station including bagging, drumming and pelletizing
- Roll Operator - One operator per roll mill
- Mixer/Grinder Operator - Operates ribbon mixers, grinders and adds compounding ingredients

- Pulverizer Operator - Dumps drums or pans of resin into grinder, operates hammermill, assists in charging area
- Shift Supervisor - Approximately 4 hours spent in production areas
- Relief and Utility Operator - Relieves operators for breaks and lunch, assists mixer/grinder and pulverizer operators as needed

The most significant exposure, although infrequent, is to airborne asbestos fibers. Asbestos was not being run during the survey, so no air samples could be collected. The following 8-hour personal sampling data have been collected by plant personnel:

<u>Date</u>	<u>Operator</u>	<u>Result (fibers/cc)</u>	
6/72	Roll	2.57	Average = 0.96
10/75	Roll	0.36	
11/75	Roll	0.74	
11/75	Roll	0.69	
11/75	Roll	2.71	
1/76	Roll	0.30	
6/72	Mixer/Grinder	3.95	Average = 0.98
11/72	Mixer/Grinder	1.93	
10/75	Mixer/Grinder	0.49	
11/75	Mixer/Grinder	0.80	
11/75	Mixer/Grinder	0.85	
11/75	Mixer/Grinder	2.00	
1/76	Mixer/Grinder	0.78	
6/72	Pulverizer Operator	1.32	Average = 0.51
10/75	Pulverizer Operator	0.31	
11/75	Pulverizer Operator	0.59	
11/75	Pulverizer Operator	0.68	
1/76	Pulverizer Operator	0.99	

These three job functions are the only ones with a significant potential for exposure to asbestos fibers. Excluding the results from 1972<sup>1</sup>, employee 8-hour exposure levels are within acceptable levels; i.e., less than 1/2 the TLV of 2 fibers/cc. The decline in exposure levels from 1972 to the recently recorded levels cannot be explained by the installation of additional or improved ventilation systems. All such systems described in the following section were installed prior to 1972. The improved control effectiveness must be a combination of improved work practices and housekeeping, proper use of external controls and a heightened awareness among employees of the seriousness of the potential hazard.

To supplement the above data, and to estimate exposures when asbestos was not used, personal samples were collected during the survey. Because many of the potential toxicants do not have TLV's or are nuisance dusts, it was decided

<sup>1</sup>The 1972 levels were within OSHA limits at that time of 5 fibers/cc.

that nonspecific gravimetric samples would provide the best index of worker exposure to this wide range of possible contaminants. The samples were collected through a cyclone assembly to collect respirable particulate matter only.

<u>Operator</u>	<u>Result (mg/m<sup>3</sup>) *</u>
Roll Operator #1	< 0.7
Roll Operator #1	< 0.8
Roll Operator #2	< 0.7
Roll Operator #2	< 0.7
Mixer/Grinder Operator	< 0.7
Mixer/Grinder Operator	< 0.7
Packout Operator	< 0.8
Packout Operator	< 0.8

\*TLV for nuisance dust = 5 mg/m<sup>3</sup> respirable fraction.

These results reflect the excellent level of dust control achieved in the process.

Sound level readings for various areas of the plant were as follows:

Roll #1 Platform	93 dBA
Roll #2 Platform	90 dBA
Crusher Room Area	80 dBA
Screening Platform	90 dBA
Ribbon Mixer Area	86 dBA
Bagging Area	85 dBA

Without noise dosimetry data, it is difficult to estimate employee time-weighted average exposure. Most operators are relatively mobile within the plant, receiving various exposure for different periods of time. Recently, the plant obtained the services of an acoustic consulting firm to provide accurate estimates of employee exposure. A 3-week survey, combining average area sound levels and an employee time and motion study, yielded the following results:

<u>Operator</u>	<u>Percent Allowable Exposure</u>
Roll Operator #1	113
Roll Operator #2	69
Bagger	5
Mixer/Grinder Operator	0
Shift Supervisor	63
Pulverizer Operator	0
Relief Operator	70
Utility Operator	0

As seen, only one job function (Roll Operator #1) has an excessive exposure. This is probably higher than the other roll area due to close proximity to

high noise level sources such as the screeners,

#### DUST CONTROL TECHNIQUES

The overall control strategy may be described under three major headings listed below:

- Local exhaust ventilation
- Work practices
- Process design, modification and maintenance

Each control segment contributes to the excellent degree of dust containment achieved in this process.

#### Local Exhaust Ventilation

Four blowers moving a total of 11.8 m<sup>3</sup>/s (25,000 cfm) comprise the ventilation system depicted schematically in Figure A.13-2. Several exhausted hold tanks, mixers and blenders are not shown because they are not now used.

The system is well designed and maintained, and several features are of particular interest:

- Transport velocities in the branch and main ducts range from 15.7 to 19.3 m/s (3100 to 3800 fpm). These high velocities are essential to keep the dust entrained in the air flow, thus preventing obstructions at duct elbows. This is particularly important considering the heavy dust loading produced by this process.
- All exhaust air is cleaned through Pulsaire cloth filter banks before being released to the atmosphere. This is good environmental practice and also eliminates the problem of dust re-entry into the workplace.
- Every potential source of significant dust generation has been provided with an adequate air flow. All hold tanks are under negative pressure, and all operations at least partially open to the workplace are fitted with tailored hoods.
- The system was dynamically balanced in the design stage. This eliminates the need for blast gate balance control, which can be incorrectly adjusted by operating personnel.
- There have been no additions or alterations to the system as originally designed. Frequently in industry, additional hoods are installed without raising the system air flow capacity.
- The charge hoods provide control for intermittent operation. When these operations are not in use, a dampering system diverts the charge hood exhaust capacity to other operations.

The exhausts for the hold tanks and the drum type mixer consist solely of a

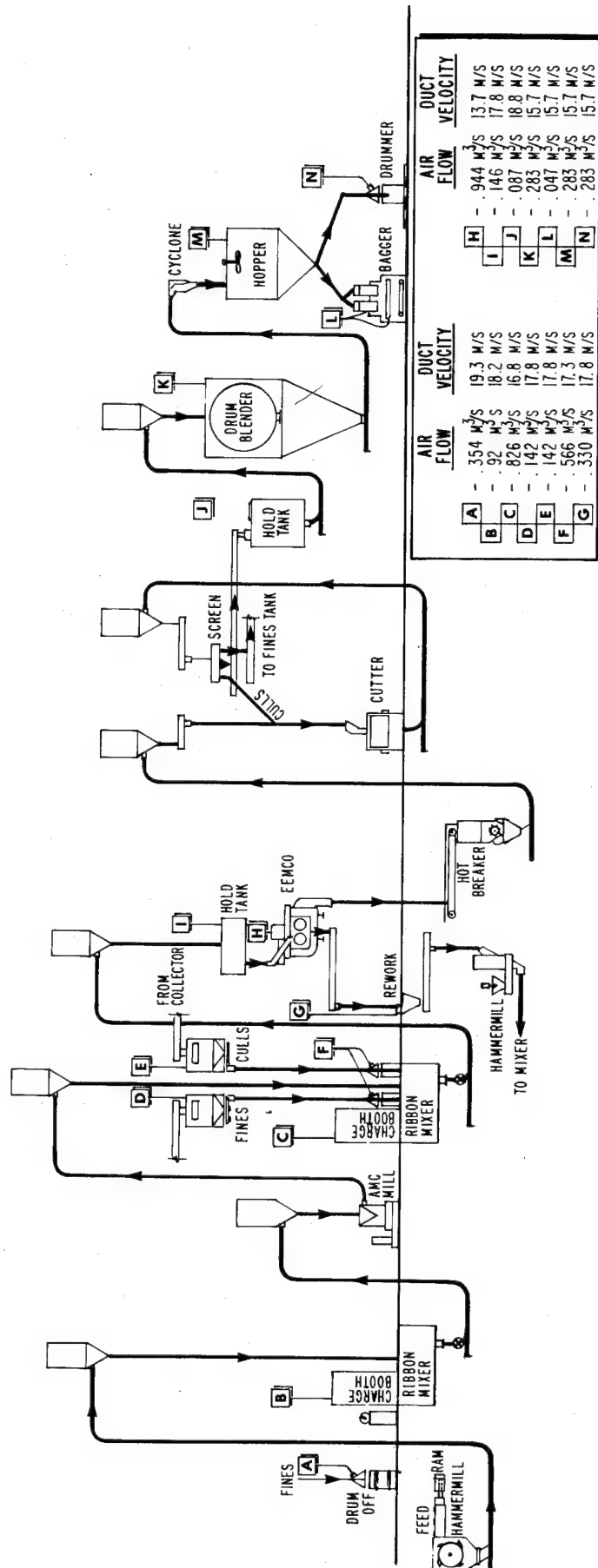


Figure A.13-2. Local Ventilation System



branch duct entering the vessel, and do not require elaboration or detailed analysis. However, the following hood arrangements are good examples of ventilation design, and are evaluated and depicted separately.

Figure A.13-3	Ribbon Mixer Charge Booth
Figure A.13-4	Discharge Hoods
Figure A.13-5	Rolls Hood
Figure A.13-6	Rework Hopper

Both the design and measured air flow parameters are outlined for each hood. A critical evaluation is similarly presented for each hood arrangement. It is noted that none of the exhaust take-offs are tapered. This lack of tapering increases the resistance to air flow and is not good design practice.

### Work Practices

Even an excellent physical control system (such as the ribbon mixer charge booths) will not be effective without the exercise of good operator work practices. For example, if bags of additives are frequently opened and spilled outside the booths, there is obviously no possibility of effective dust containment. Proper work practices are an essential adjunct to an optimum process design and the external control system.

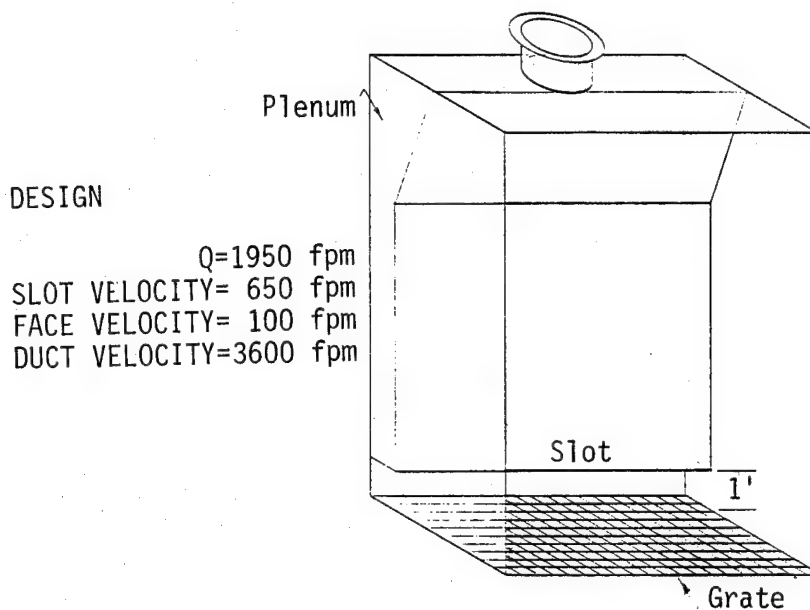
For this compounding process, the dry additives operation requires well conceived work practices and is analyzed below. Other operations do not require the same degree of operator interaction, and thus are not included in this discussion.

#### Ribbon Mixer Charge Booths--

As mentioned before, even with the well designed charge booths, extensive workplace contamination can occur without strict operator adherence to a structured charging methodology. Through observation and discussions with operators and supervisors, it was learned that the following procedures are used for dumping dry additives.

- Bags are positioned directly in front of the charge booth.
- One at a time, they are placed over the grate, slit open, turned over and dumped into the mixer.
- The empty bags are purged of residual particulate matter by vigorous shaking directly in front of the exhaust slot.
- Depending on the contents, the bag is either dropped into a polyethylene-lined container (asbestos only), or flattened and baled inside or outside of the booth.
- Any spillage is swept into the booth.

Partial or short weight amounts of additives present special problems. Fortunately, these are relatively infrequent and short-lived. Most short weight quantities involve half bag weights. In these cases, the bags are slit into two equal sections, one is dumped and the other is carried to the scale and



The four charge booths serve the dual purpose of controlling dust when dry additives are dumped and when the resin is charged into the mixer. The latter purpose is particularly important because a large amount of dust-laden air is displaced by the charged resin and exits through the dump grate.

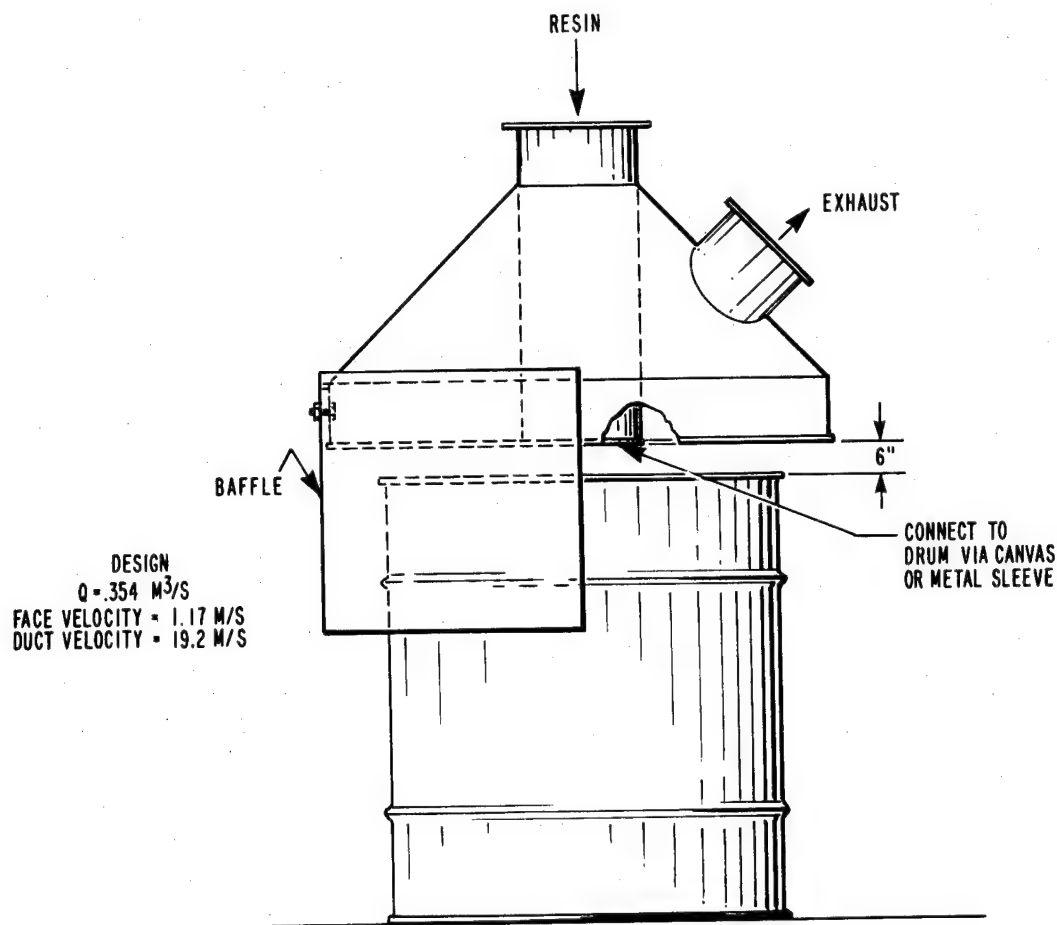
Air flow measurements taken during the survey revealed slot velocities ranging from 3.56 to 7.62 m/s (700 to 1500 fpm). These are higher than the design slot velocity of 3.30 m/s (650 fpm) because the slot height has been reduced and several discharge hood exhausts were dampered.

Due to the placement of the slot, face velocities were non-uniform, ranging from 1.52 m/s (300 fpm) at the bottom to <0.25 m/s (<50 fpm) at the top.

Desirable features:

- 1) The booths are deep enough (.914 m [3 ft.]) to reduce cross draft turbulence in the capture area.
- 2) The non-uniform face velocity profile results in high velocities in the dust generation area where they are needed.
- 3) The high slot velocities allow empty bags to be purged of residual additive particles prior to removal from the booth.
- 4) The booths are large enough to allow temporary storage of partially filled bags and baling of empty bags.
- 5) The exhaust induces a slight negative pressure on the mixers, resulting in a reduced potential for dust leaks.

Figure A.13-3. Ribbon Mixer Charge Booth



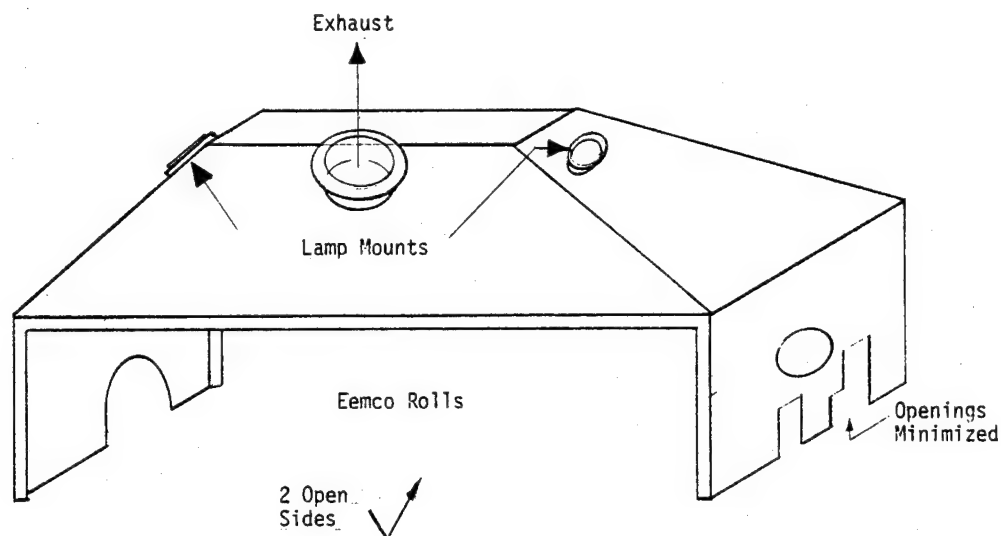
The discharge hoods provide control for three separate operations: fines drum-off, resin charging and final product drum-off.

Air flows ranged from .273 to .359  $\text{m}^3/\text{s}$  (580 to 760 cfm) estimated by duct velocity measurements. Measured face velocities were roughly equivalent to the design value of 1.17 m/s (230 fpm).

Desirable features:

- 1) The semi-circular baffles are essential to effective dust control by reducing adverse effects of cross drafts and limiting open area (resulting in higher capture velocities).
- 2) The hoods are installed to fit closely (15.24 cm [ $<6$  inches]) over the top of the barrel or drum. This also reduces open area and affects an increase in capture velocity.
- 3) The resin chutes can be extended into the drums, using canvas or metal sleeves. For several applications, the top of the drums can be closed around the sleeve or canvas.

Figure A.13-4. Discharge Hood



#### DESIGN

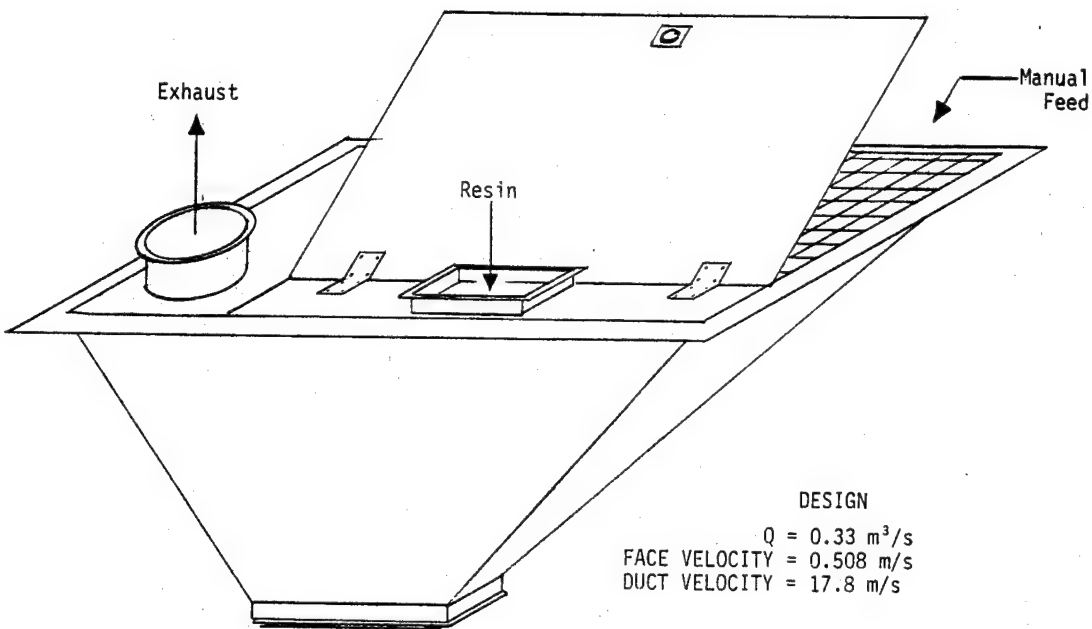
$Q = 0.944 \text{ m}^3/\text{s}$   
 FACE VELOCITY  $\cong 1.02 \text{ m/s}$   
 DUCT VELOCITY =  $18.8 \text{ m/s}$

Simple canopy hoods provide exhaust for the two rolls. The measured face velocity ranged from .508 to .762 m/s (100 to 150 fpm) which is somewhat lower than the design value of 1.02 m/s (200 fpm). Because the exhaust duct was dented in several places around an elbow, it is assumed that the lower air flows may be caused by partially plugged ducts. It would be desirable to install a clean-out opening at these elbows. However, sample results and observations indicate that the existing face velocities are adequate.

#### Desirable features:

- 1) The two side panels fit directly on the mill housing with only small open areas. If these two sides were open, the face velocity would be reduced by over 33%.
- 2) The canopy hood design takes advantage of the convection currents induced by the hot rolls.

Figure A.13-5. Rolls Hood



The hopper exhaust provides control when resin culls are dropped from the rolls and/or when other rework resin is manually charged to the hopper.

Desirable features:

- 1) Since manual rework charging is infrequent, the feed hatch is usually closed, and the hopper is under a relatively large negative pressure.
- 2) When the feed hatch is open, the design face velocity ( $0.508 \text{ m/s}$  [100 fpm]) is sufficient to prevent the escape of the dust.

Figure A.13-6. Rework Hopper

weighed. Based on this measurement, small quantities are added until the proper recipe weight is achieved. It is believed that, if short weight operations were most frequent and lead or chromium pigments were used (asbestos is apparently not short-weighted), an exhausted scale facility would be necessary.

Major spills from leaky pallet loads are vacuumed up immediately. The success of these practices can be traced to strict, continual training and close supervision. It was quite apparent that everyone knew that non-adherence to proper procedures and sloppy operations would not be tolerated.

Due to its toxicity, asbestos requires special consideration. Pallet loads of asbestos bags are encapsulated in polyethylene to lessen the potential for leakage and to maintain bag integrity.

#### Housekeeping--

Although good housekeeping may be considered separate from work practices, it is included in this section because of its importance to proper control. Observations revealed that operators spend a considerable amount of their time cleaning. The benefit of this activity is apparent in the low measured concentrations of airborne dust. Every two weeks, the entire plant (including surfaces such as rafters) is thoroughly vacuumed. Basically, this means that settled dust never has a chance to accumulate sufficiently to become a significant secondary source. The plant is provided with a series of strategically located connections into a suction air system. Long flexible hoses are hooked into the system allowing vacuum coverage to essentially all plant areas.

With the exception of the exhausted operations, control is affected by the closed nature of the system. However, dust leaks can be quite common in this type of operation, particularly in the flexible junctions or "boots" connecting process equipment with the air conveyance systems. It is not unusual in industry for totally enclosed operations such as screens to be excessive dust sources due to leaking connector boots. This plant copes with this potential problem by frequent inspection of all boots or other weak points in the otherwise closed system. Work orders are dispatched and repairs completed well before minor leaks become major dust sources.

Furthermore, the plant is shut down twice a year for a complete equipment inspection, needed maintenance operations and a thorough cleanup. These temporary disruptions in production are apparently well worth the effort because of decreases in unplanned shutdown and the concomitant potential for dust generation.

#### Process Design and Modification

The plant is relatively new and it is quite apparent that it is well designed and laid out. Some of the aspects of the design that affect dust control are:

- Closed System - Quite simply, there are very few unit operations with openings to the workplace. Material is transported exclusively by airveyor or closed screw conveyor. Many unit operations, such as the Durez Hot Breaker or the Loomis Hammermill, are completely isolated and employees are rarely in these areas. The process is not labor intensive; several operators

can monitor and run the entire plant.

- Pneumatic Conveyor - Most of these transfer lines convey large masses of relatively large resin particles. Substantial impact friction forces are directed at elbows, where this heavy material must change direction. Without protection, small holes can occur and, for positive pressure systems, the resin particles can escape to the workplace. Durable sleeves have been installed around all elbows on positive pressure pneumatic conveyor lines with good success. The sleeves are Shelby LG Sweep Elbows, with removable backs and urethane lining.

#### PERSONAL PROTECTIVE EQUIPMENT

Respirators are only required when asbestos is being used. Employees charging the asbestos wear 3M disposable gauze respirators.

Employees working with asbestos are also required to wear coveralls, which remain at the plant for laundering.

Ear plugs are worn by the roll operators.

#### APPENDIX A.14. A GENERAL DESCRIPTION OF COMPOUNDING CONTROLS

Seven compounding operations were evaluated by walk-through surveys during the course of the study. All seven operations were part of large polymerization plants with compounding integrated into the overall process. Of these, only one (presented previously in A.11) was acceptable for a study of effective engineering controls and work practices. Although seven compounding facilities out of a very large industry are inadequate samples, it is judged that these facilities are typical of others in the industry. Since the controls utilized in the seven processes were judged ineffective, detailed studies were not undertaken. However, a general evaluation of observed deficiencies and suggested improvements is presented below.

##### GENERAL EVALUATION OF COMPOUNDING OPERATIONS BASED ON WALK-THROUGH SURVEYS

###### Toxic Chemical Agents and Harmful Physical Stresses

The number and complexity of the various compounding ingredients commonly used are staggering. Many of these materials were observed being used in the compounding facilities which were surveyed. Several overall comments are necessary:

- The use of toxic metallic pigments (lead, cadmium, chromium) was widespread.
- Many times the compounding additives used are trade name custom blends, with no information (other than general warnings) on the chemical make-up of the additives. A general impression is that it is frequent for plant personnel to be unaware of the exact nature of potential exposures.
- It would be exceedingly difficult to evaluate control effectiveness and potential employee exposure based on short-term surveys. It is common for compounding recipes to be changed after every batch. Without long-term sampling programs, it is impossible to accurately estimate anything other than peak exposures.
- With only a few exceptions, the compounding plants visited have yet to initiate any air sampling program.

##### ENGINEERING CONTROL AND WORK PRACTICE EVALUATION

###### Toxic Chemical Additives

The operations which are major sources of toxic dust generation are raw material handling and storage, additive weighing and batch recipe make-up, additive entry into mixer or blender, all mixing and blending operations up to the operation where the additives are fused into resin, and all hoppers and material transfer systems. Some of the more common problems leading to excessive exposure that were noted during the surveys are:



- Inadequate general ventilation: Many of the toxic materials used are in the form of very fine powders, with particle sizes below 5 microns mean aerodynamic diameter. When these particles become airborne, they will remain suspended for extremely long times unless removed by an adequate general ventilation system.
- Poor housekeeping: In most cases, there is no scheduled cleanup in areas where toxic materials are used. In essentially all cases, when cleanup is undertaken, dry methods such as sweeping are used. Further, employees frequently use compressed air to rid their work areas and their clothing of settled dust. Both of these cleaning methods are disastrous in terms of dust control; it is probable that no cleanup is preferred to these methods.
- Improper storage and handling of toxic additives: Few compounding facilities had segregated and/or limited access storage areas for toxic additives. Frequently, pallet loads of additive bags and containers were positioned in large, open storage areas where they may be torn or ripped by fork lifts, etc. Further, spills of dry material will readily become airborne due to frequent equipment or personnel movement. There were numerous examples of open containers of toxic materials being transported or stored in open containers (i.e., half bags, plastic cups). A significant amount of airborne dust, particularly from fine powder additives, results from this practice. Finally, common practice of handling empty additive bags is to compact them by hand in a non-exhausted area, dump them in open trash barrels, and/or leave them on the floor until picked up and disposed of as other trash. Any of these practices are large sources of potential exposure.
- Poor work practices: When using toxic, dry materials, proper work practices are critical to successful dust control. Examples of poor practices observed during the survey include opening additive containers outside of the hoods provided for dust containment, sloppy handling of additive powders, poor opening procedures for bags, and general improper use of local exhaust systems. Most times, additives were received in 50 pound to 100 pound bags although batch recipes normally require much smaller quantities. This requires an expanded amount of short-weight additive preparation.
- Nonexistent or poorly designed local ventilation systems: Compounding plant local ventilation ranged from one job shop compounding plant with none to an exceptionally well designed system that was so poorly maintained that it was not effective. Most plants had either table top or walk-in hoods where additives could be weighed out in accordance with batch recipe requirements. Without exception, all were of poor design, including: 1) inadequate design airflows; 2) ineffective placement and sizing of exhaust slots; 3) low duct transport velocities which lead to plugging; and, 4) too shallow hood depths. Further, many hoods were swept with excessive cross drafts, either from pedestal fans or open windows. The hoods designed to exhaust the additive dumper operation into the mixers and/or blenders were similarly poorly designed.

Most mixers, blenders, hoppers, feed chutes and conveyor belts were not provided with any local ventilation. A substantial amount of dust is generated when seals wear out and fittings are inadequate.

- Poor ventilation system maintenance: With dusts, particularly where the exhaust loading is heavy, maintenance of the local ventilation system is essential. If duct transfer velocities are not maintained at 17.78 to 20.32 m/s (3500 to 4000 fpm), dust particles will not remain entrained in the air flow. Most of the time, this occurs at branch elbows, and the duct gradually becomes obstructed and air flows are choked or at least diminished relative to design values. This situation appeared to be quite common at surveyed plants because, in general, air flows were well below minimum accepted values.

Most local ventilation systems designed to remove dust have particulate filters in line to allow exhausting of relatively clean air to the atmosphere. With heavy dust loading, the filters will rapidly become plugged, due to the increased system static pressure (resistance). The actual air flow will decrease to values well below the value specified on design. It was a frequent observation that the filters are not monitored to determine when maintenance is required.

Finally, no plant had suitable sampling equipment available to periodically monitor air flows to assure effectiveness.

## CONCLUSIONS

Based on the site visits to compounding plants, it is concluded that effective examples of engineering controls and work practices are not widespread. The problem is that, while numerous recommended ventilation controls exist in the literature, many are contradictory, are not based on proven scientific principles, and may easily lead to inadequate control of operations.

A previous NIOSH study (1976) has thoroughly investigated the literature relative to engineering controls for operations handling dry materials. The sections of the study dealing with the control of compounding process exposures are abstracted below, including a brief review on the literature relative to control technology.

Exposure Source: Emptying of Bags and Drums

Controls--

- Excellent hood arrangement in Case Study 13
- Exhaust arrangement for dumping 50-pound bags of fine pigment powder using "flip top" arrangement (Owen)
- Hood designs for emptying bags into open top mixers and mill loading spot; includes lateral draft hood design alternative; describes methods for weighing and mixing amounts of highly toxic materials (Stern and Horowitz)
- Successful procedures for handling lead compounds in PVC compounding plant (Goss and Ross)
- Flexible metal hose systems for loading container not permanently placed; also method for charging open mixers (Hemeon)

- ACGIH Industrial Ventilation Manual describes exhausted booth for manual loading of hoppers - open front booth with rear exhaust pulling  $.071 \text{ m}^3/\text{s}$  ( $150 \text{ cfm}/\text{ft}^2$ ) of face area
- Steel Mill Ventilation recommends capture velocity of  $.762$  to  $1.02 \text{ m/s}$  ( $150$  to  $200 \text{ fpm}$ ) for openings in bind and hopper enclosures
- Enclosed and ventilated bag opening station which is largely automated (Goldfield and Brandt; Hills)

Exposure Source: Bag Filling

Controls--

- Three-sided booth enclosure with plexiglass window and hinged plate edging on front edge of floor (Hama)
- Bag filling hood and bag tube packer (ACGIH Industrial Ventilation Manual)
- Recommended airflows for hooded bag filler from pulverizer, hood enclosures for bag packing, pouring slot for bag filling, hood over bag packing from belt packer (Constance)
- Various bag filling machinery available to chemical industry (Burke)

Exposure Source: Drum Filling

Controls--

- Excellent hood designs in Case Study 13
- Four hood systems for barrel filling (ACGIH Industrial Hygiene Manual)

Also included in NIOSH study (1974) is a review of controls used for belt conveyor transfer points, belt conveyor straight runs, drag conveyors, enmasse conveyors, flight conveyors, pan conveyors, pneumatic conveyors, screw conveyors, vibrating conveyors, pivoted bucket conveyors, bin filling, bucket elevators and chutes, pouring stations for liquids and a brief dissertation on package integrity.

## NOISE

In general, excessive noise exposure in compounding plants is limited to the area around the pelletizers and dicers. Noise levels in these areas commonly range from  $100 \text{ dBA}$  to  $115 \text{ dBA}$ . It was apparent from the walk-through surveys that despite some effect at noise abatement, most pelletizers and dicers remain significant sources of employee exposure. The problems are varied:

- Several compounding plants have built concrete block rooms around the pelletizers. Although these structures provide adequate attenuation through transmission loss, the openings are usually too large, doors are frequently left open, and the enclosure provides no protection when employees must enter the room.
- Noise abatement measures applied directly to the pelletizer have not been successful because the sources of noise are numerous and complex, and the controls significantly interfere with frequently required maintenance operations.

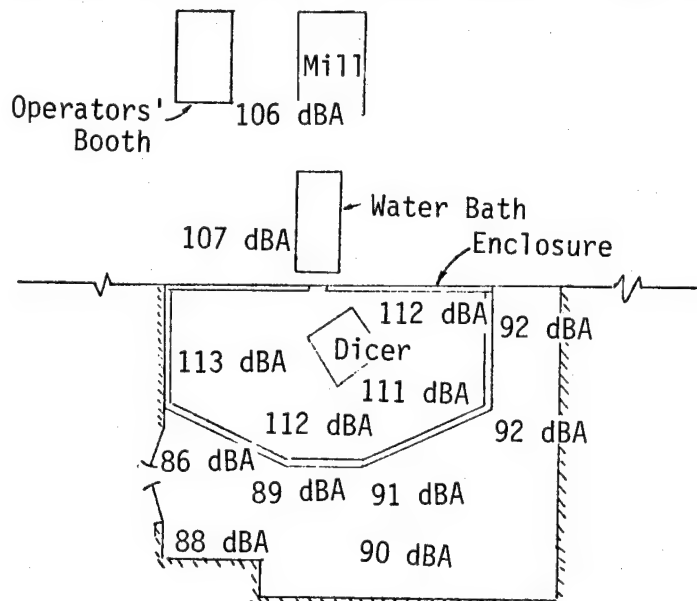
- Noise abatement packages offered by pelletizer manufacturers (Cumberland Engineering Co., etc.) are effective to some extent, but are not used because they are very expensive and substantially impede maintenance operations.

One potentially successful enclosure design:

<u>Application</u>	<u>Noise Control Equipment</u>
Cumberland Dicer 14" Stair Step Model	Room enclosure for dicer. Ceiling, walls, doors and windows manufactured by Industrial Acoustics Company, Bronx, New York

The Cumberland dicer is one of four located at the end of adjacent product lines. The acoustical enclosure is being tested on the one dicer before being installed on all four lines.

Construction details of the enclosure are available from the manufacturer. Noise level readings were taken with all other product lines down to estimate the effectiveness of the enclosure. The results are shown below:



In the room housing the dicer enclosure, the noise results indicate that enclosure provides an attenuation of about 22 dBA. Exposure in this area would still be marginally excessive.

Of major concern are the noise levels (107 and 106 dBA) outside the room, near the water bath and the mill. The noise attenuating effect of the enclosure is being completely negated, due to an excessive chute opening for passing the resin strand into the enclosure. For this noise control enclosure to be effective at all, the opening will have to be reduced drastically. Further, a 3 to 4-inch acoustically-treated, four-sided tunnel will have to be fabricated and installed from the feed chute outward towards the water bath. The tunnel should include a series of acoustically-treated baffles and, if possible, should not have direct line of sight from the enclosure outward.

## APPENDIX A.15. MONITORING INSTRUMENT SYSTEM EMPLOYING A FOURIER INTERFEROMETER

### INTRODUCTION

A more recent development in monitoring instrument systems is the use of an area monitoring system for computing time-weighted average exposure in real time. This monitoring instrument system consists of a Fourier Infrared Composition sensor for measuring VCM concentration levels in air samples, a sample collection manifold, a digital computer, output equipment and software that combines a data processing algorithm and a statistical model of a time and motion study of plant operators' activities. This system was installed in a PVC resin manufacturing plant employing the suspension process. A block diagram of the system is shown in Figure A.15-1.

The sampling manifold collects the samples and makes them available for analysis by the infrared interferometer sensor. An on-line computer activates the sampling manifold to deliver desired area samples of breathing air to the sensor. The sensor output is analyzed by the on-line computer, the exposure data is printed out when requested, and the annunciators are activated when permissible exposure levels are exceeded.

### DESCRIPTION OF PVC PRODUCTION FACILITY

#### The Physical Plant

The production of PVC resin is carried out in two separate buildings referred to in this discussion as Plant #1 and Plant #2. Plant #1 contains six reactor vessels and Plant #2 contains fourteen.

Each plant building has an upper and a lower level. The upper floor level is high enough to allow operators access to the tops of the reactors and to the various controls and valves used to operate the process. The lower level is utilized when the reactor contents are transferred to other points in the process. The plot plans for the upper and lower levels in Plant #1 are shown in Figures A.15-2 and A.15-3 respectively. For purposes of this discussion, details will be given only for Plant #1. Plant #2 is larger but similar.

#### Worker Exposure

Following the promulgation of the temporary emergency Federal standard for vinyl chloride, the two plant buildings were characterized for VCM levels and worker location. It was possible to make this characterization quantitative because the process is highly systematized in terms of time and motion and independent of the variations in work habits of individual workers.

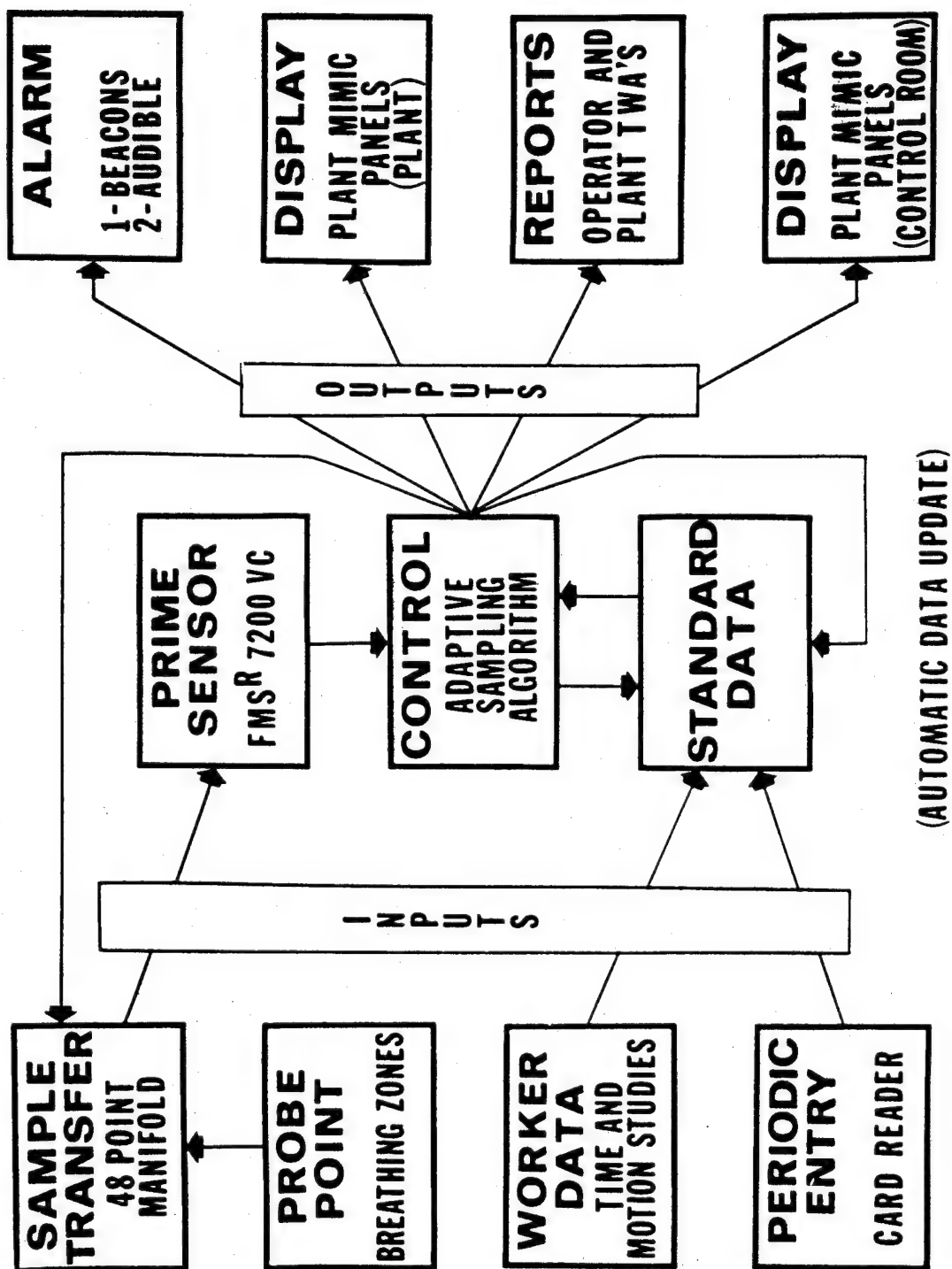


Figure A.15-1. Block Diagram - VCM Monitoring System

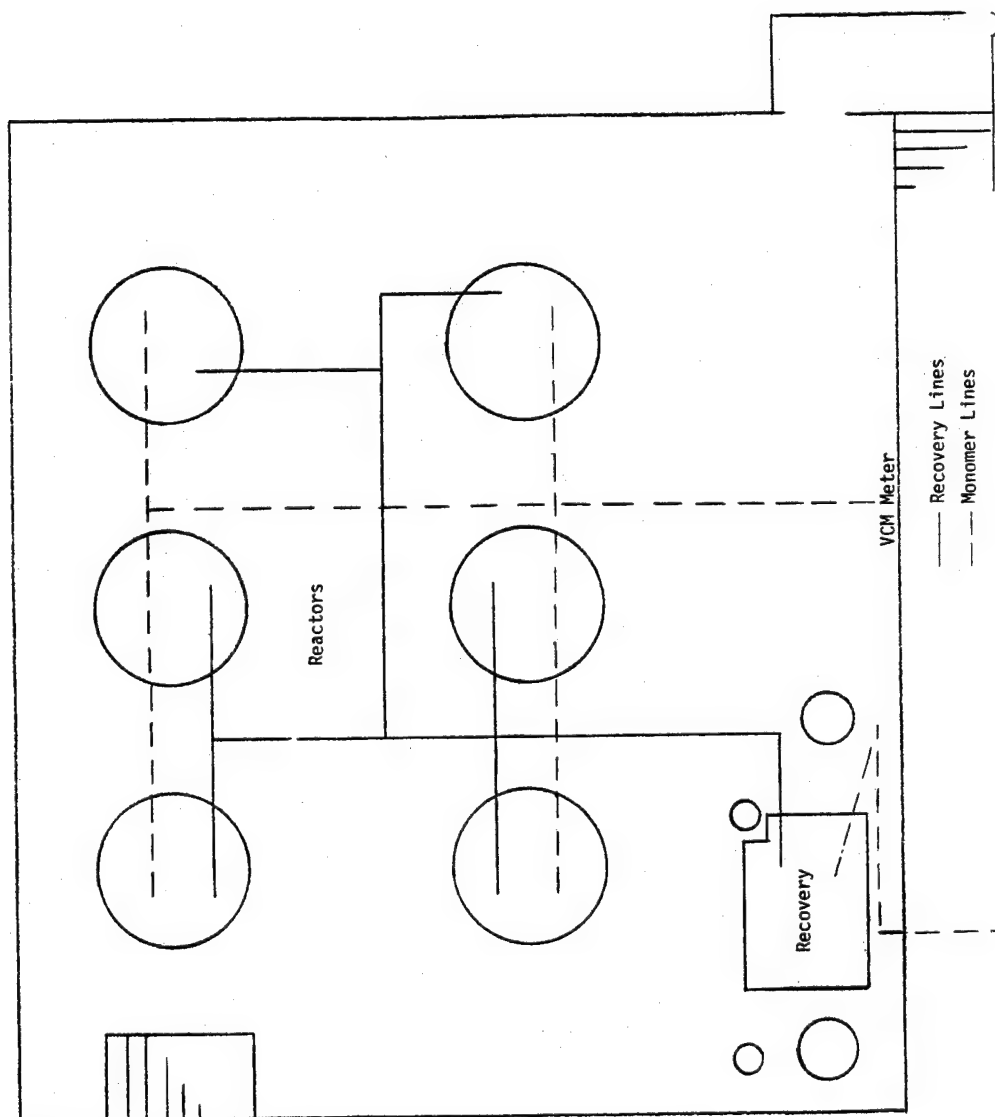


Figure A.15-2. Plot Plan Upper Level - Plant #1

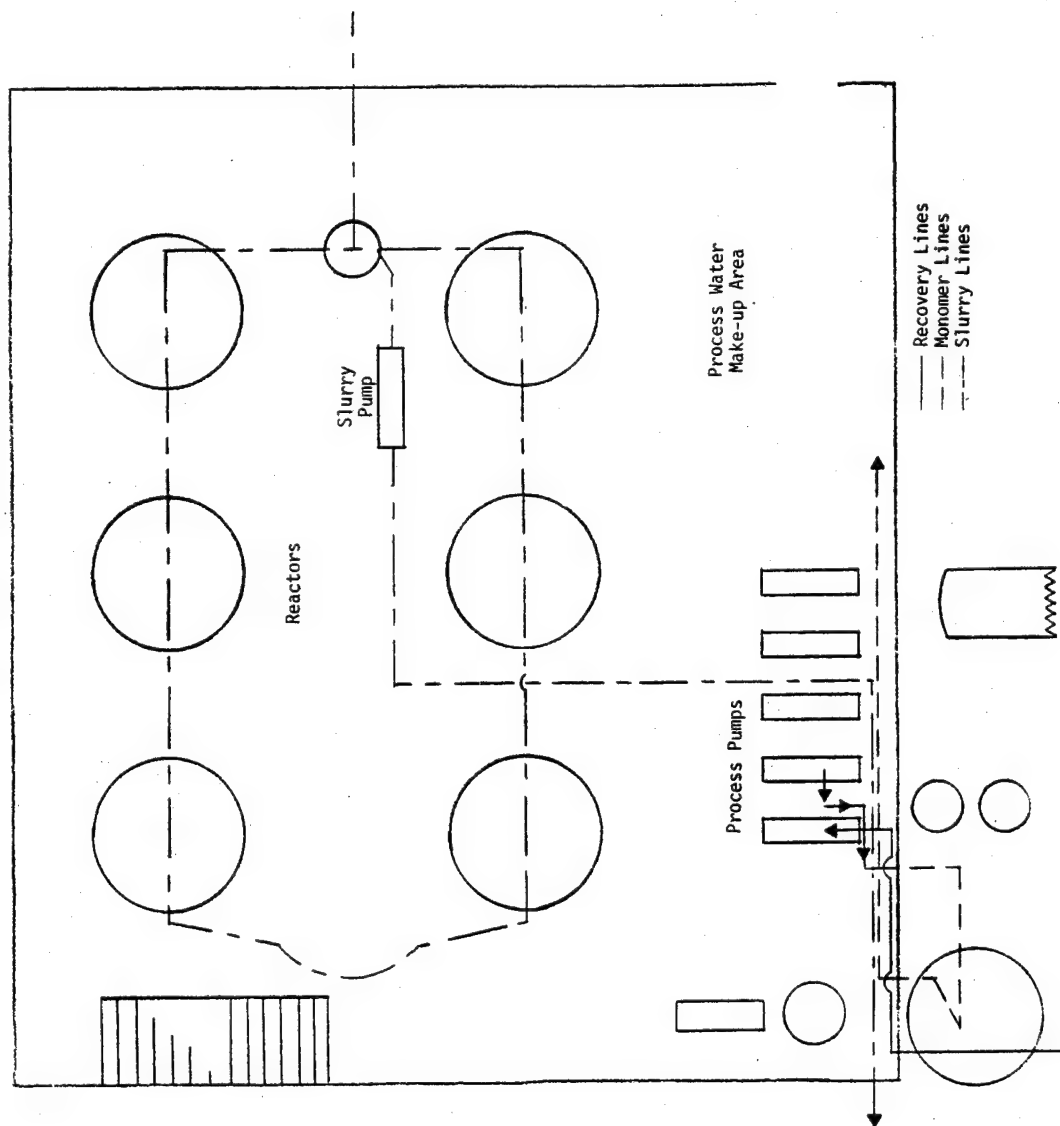


Figure A.15-3. Plot Plan Lower Level - Plant #1



To systematically describe the worker environment in quantitative terms, each plant is subdivided into logical areas or regions for study. Each of these regions is about 100 feet<sup>2</sup> in area and logically located around process equipment. Two types of determinations were made for each subdivided area. In the first determination, the probability of VCM excursions in excess of 25 ppm were made by monitoring each region at five locations within the region. A portable infrared analyzer equipped with selectable valve and six-point sampling probes was used to monitor VCM levels within each region. The sample probes were set up in locations that approximated breathing zones. Typical probe locations were at valves, charging manifolds, manways, aisle space, etc. A determination of the probability of a VCM excursion over 25 ppm as a function of time was made for each region during sixteen hours of testing in each region. Figure A.15-4 shows the location of probes at the upper level of Plant #1 and Figure A.15-5 lists the probability of a VCM excursion equal to, or greater than, 25 ppm.

After the preceding measurements were taken, time and motion studies were undertaken to determine the probability that an employee with a specific job classification would be in a given plant region. Figure A.15-6 lists the probability of a man being in a work area as determined by a time and motion study.

#### SAMPLE TRANSPORT SYSTEM

The sample transport system<sup>1</sup> consists of a 48-point sample manifold, and a pumping and valving arrangement that delivers air samples to the sensor sample cell. The computer selects the point to be sampled and the air sample is "pulled" by the sample pump through the sample cell. All sample lines not being monitored are under a constant vacuum to assure that fresh samples are available when needed for analysis.

The 48 sample probes are connected in split probe arrangements of two or three to 23 sample lines. A typical split probe arrangement is shown in Figure A.15-7.

This split probe arrangement averages the VCM level readings and typically reduces the analysis time per typical probe. For example, if the concentration of VCM in the split probe arrangement is less than 1/3 of the permissible VCM level when the samples are averaged, the computer will select another probe arrangement for analysis. However, if the reading is greater than 1/3 of the permissible VCM level, the computer will command that VCM analysis be performed on air samples from individual probes within the arrangement in order to identify the zone where VCM concentrations are excessive. The probes located in the upper and lower levels of Plant #1 are grouped in the arrangements shown in Figure A.15-7. Probes located in Plant #2 are distributed in a similar pattern. The manifold of the sample transport system is located centrally between the two plants so that the sample lines have lengths varying between 30.48 and 182.9m (100 and 600 feet).

---

<sup>1</sup> The sample transport system is available from the Pantasote Company of New York, Inc., Passaic, New Jersey.

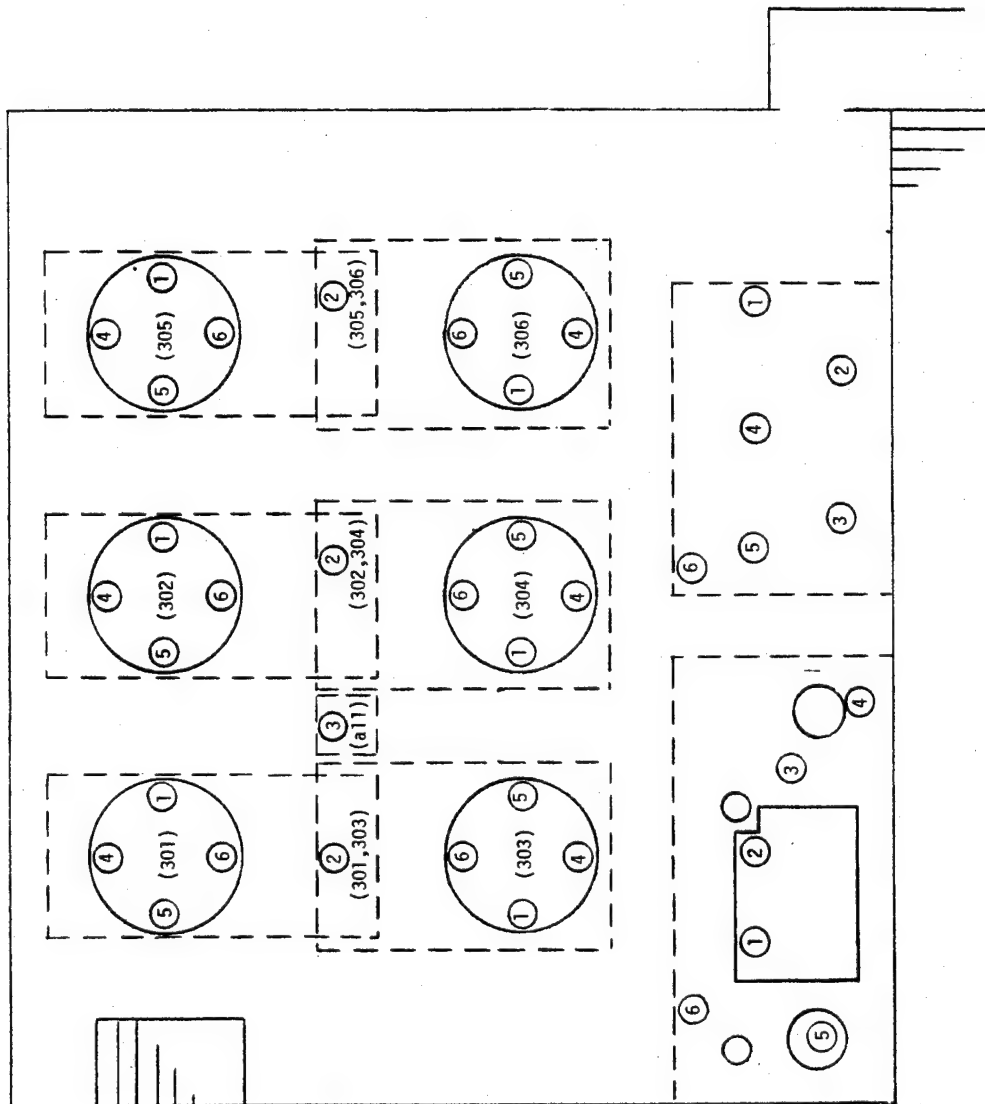


Figure A.15-4. Location of Test Probes - Six-Point System - Upper Level - Plant #1

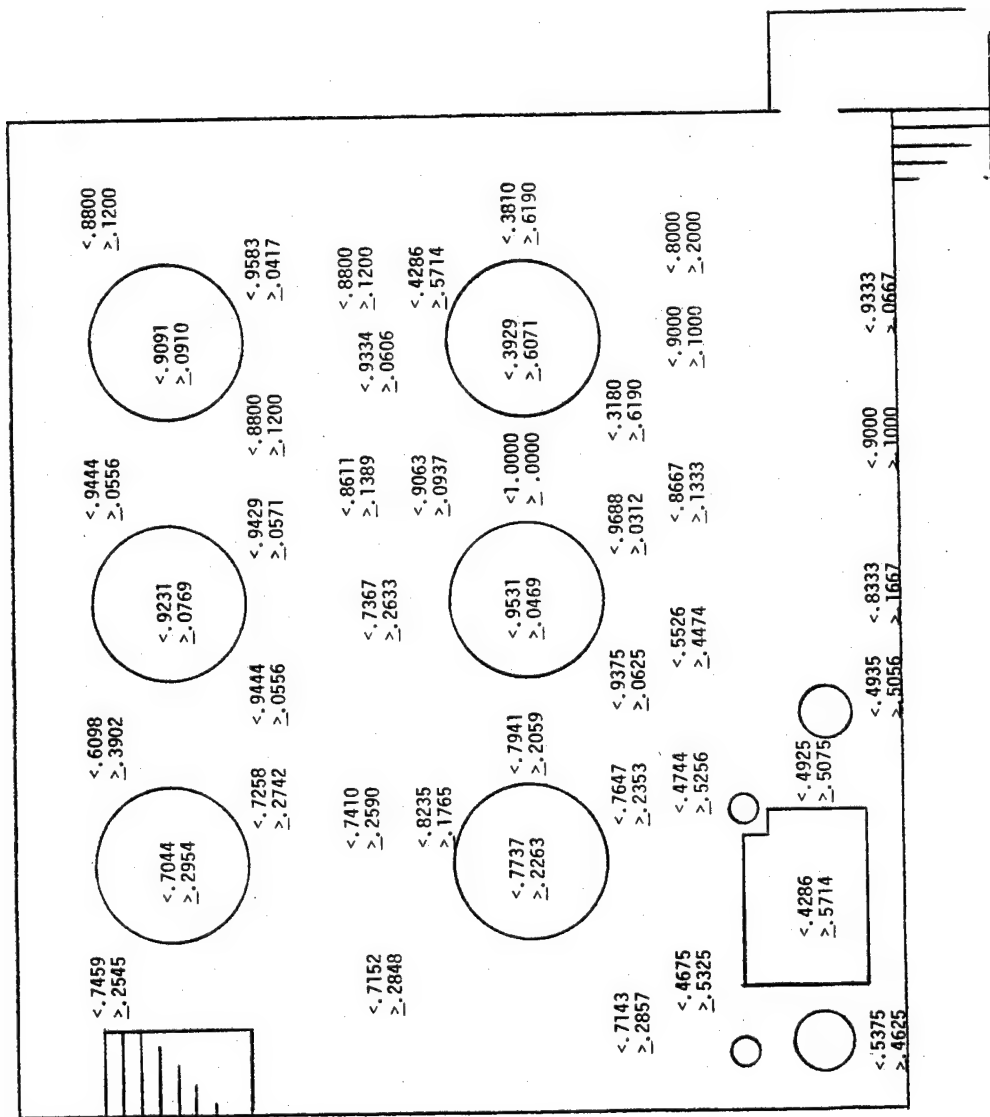


Figure A.15-5. Probability of an Excursion Above 25 ppm - Upper Level - Plant #1

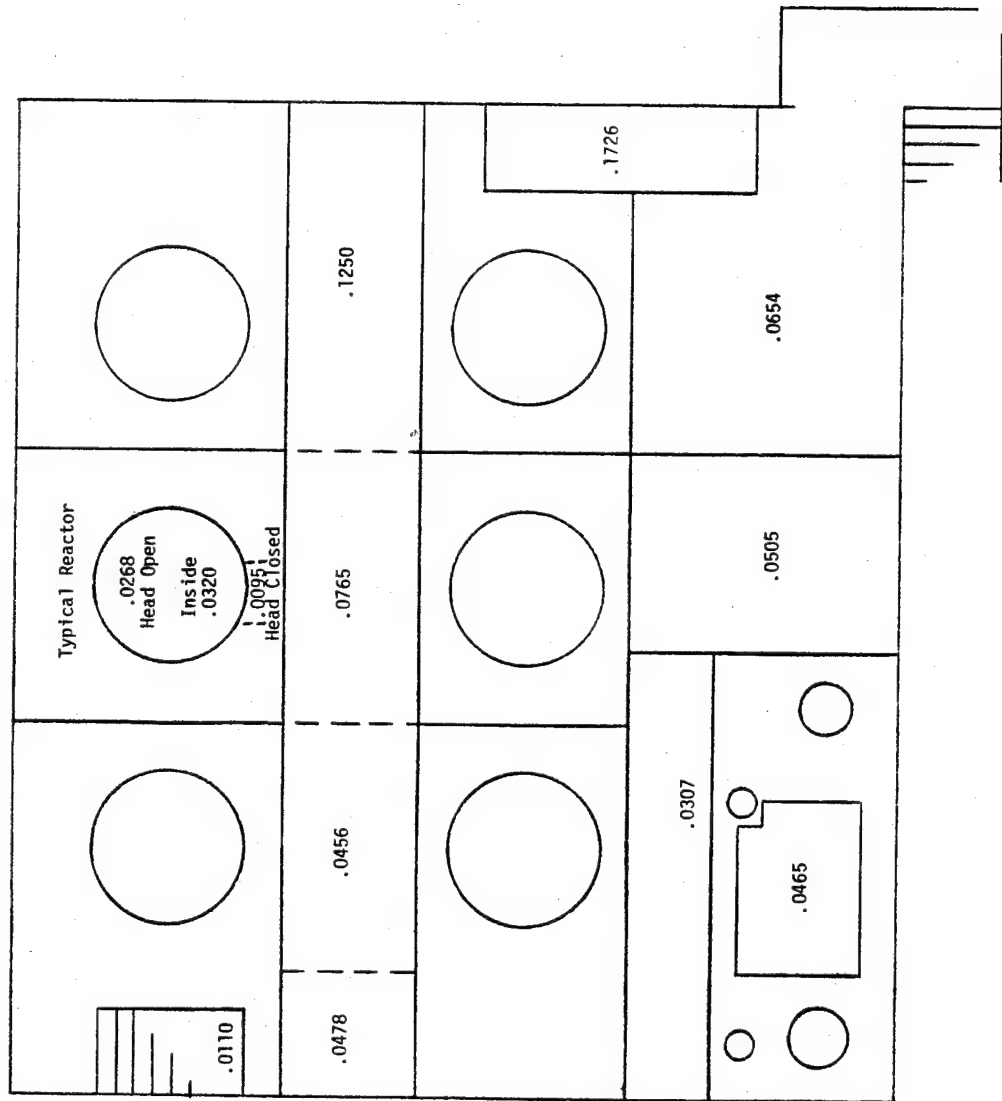


Figure A.15-6. Probability of a Man in an Area. (Results of Time and Motion Study)

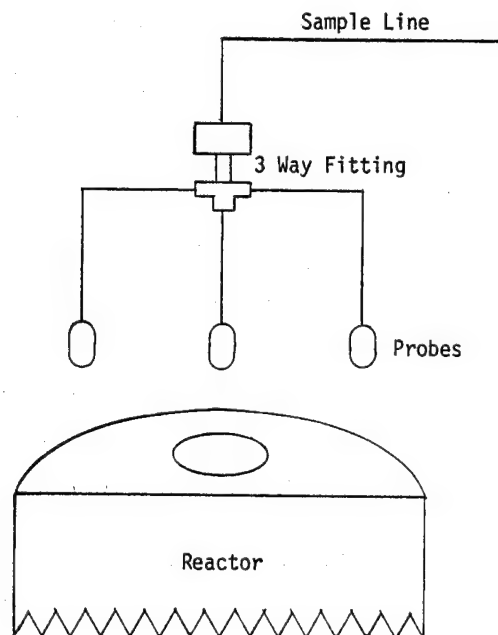


Figure A.15-7. Sample Transport System

#### DESCRIPTION OF COMPOSITION SENSOR

The composition sensor is a rapid-scan Michelson interferometer. Its electrical output is coupled to a high-speed digital computer. The air sample can be scanned for several components in about 15 seconds. Software performs classical Fourier transforms on selected frequencies in real time. The above system is marketed as the Fourier infrared air monitor. The system used at this plant is manufactured by Ecom Corporation (Fourier Multiplex Spectrometer System Model 7200).

#### SYSTEM SOFTWARE PACKAGE

Additional software was developed to meet the following requirements for an intelligent multi-level sampling system:

- Determine the frequency and level of sampling to be initiated at each station.
- Isolate the alarm level excursions and display the results.
- Provide the data for the computation of accurate employee TWA's.
- Update the internal data file to reflect the general changes in vinyl

chloride levels at the points being monitored.

A sampling algorithm was developed to sample groups of stations over a period of time in proportion to their probabilities of having points with extremely low probability of excursion. The sampling algorithm and the statistical model of time and motion study are used to compute the employee time-weighted average exposures.

A plant report listing the following information is printed every 15 minutes:

- Number of blue alarms ( $\geq 5$  ppm  $\leq 24$  ppm)
- Number of yellow alarms ( $\geq 24$  ppm  $\leq 1000$  ppm)
- Number of red alarms ( $\geq 1000$  ppm)
- Average TWA of the plant over report interval
- TWA dosage of each operator over report interval

Also, at the end of eight hours, the following reports are generated:

- Long-term TWA
- Average length of each alarm
- Probability of each alarm level

Initial start-up and definition of plant configuration requires manual operation. Thereafter, the system will define the plant profile, calculate TWA's, initiate alarms and update its data files.

This intelligent monitoring system has the following distinct advantages over fixed-point monitors:

- The monitoring system responds to the plant environment.
- Sampling frequency is determined by the probabilistic history of the point in question, using data accumulated over the previous eight hours.
- The system hunts for excursions using its probabilistic intelligence.

The following tests were carried out to establish the equivalency:

- Charcoal tubes changed once per hour monitor at one of the area probes and the results were compared with the TWA data from the area monitor.
- Monitoring four employees with personal monitor using charcoal tubes for one-hour intervals for a total of 21, 8-hour work shifts.

A comparison of the data from the first test (Figure A.15-8) shows a good agreement of both methods with the expected log normal distribution curve.

Readings from the second test (Figure A.15-9) show the area monitor data follows the log normal distribution curve while the charcoal tube data does not. This is accounted for by the fact that employees are not always in the plant. Allowing the time motion study to bias the employee out of the plant automatically is now in practice.

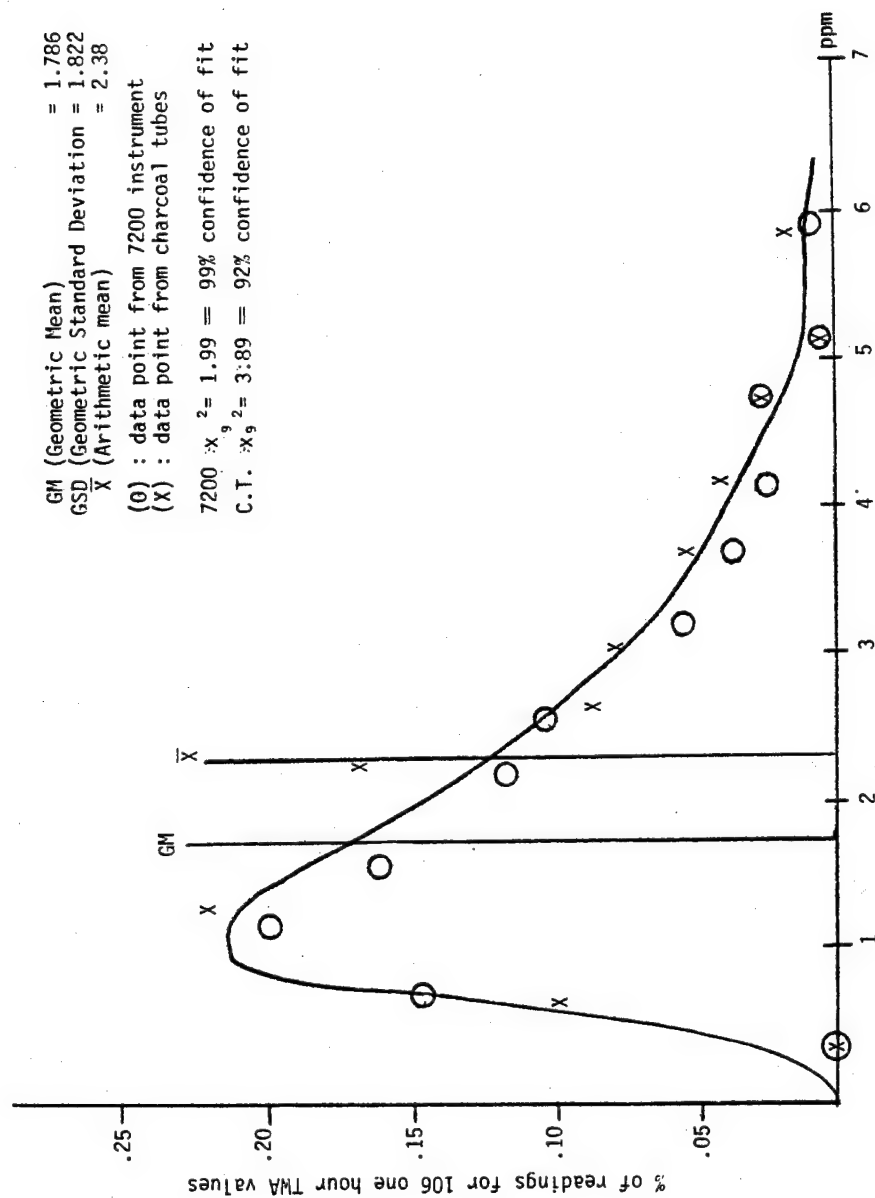


Figure A.15-8. Observed Airborne VCM for a Fixed Point in the Plant



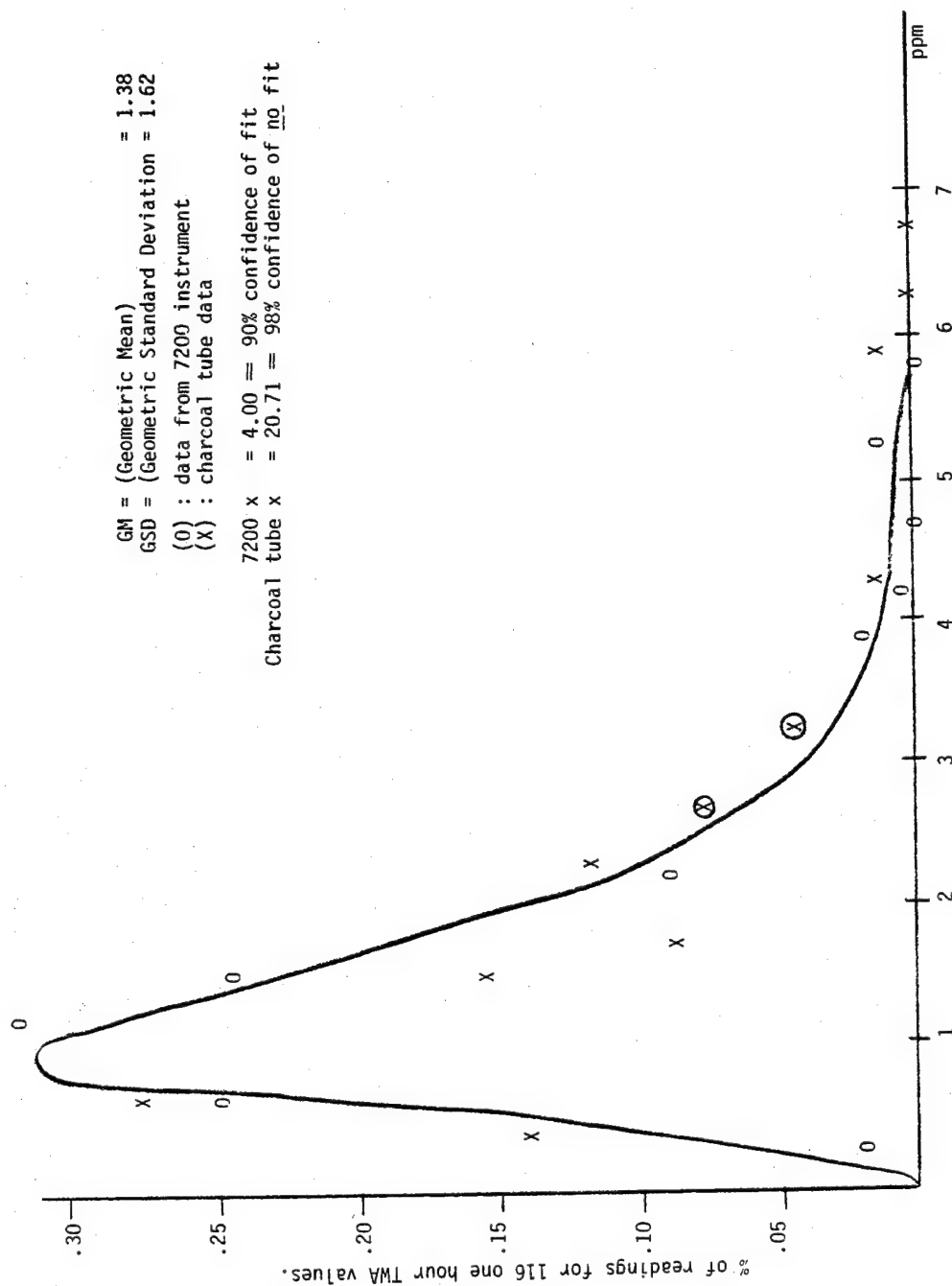


Figure A.15-9. Employee VCM Exposure for Typical Work Month

## APPENDIX A.16. MONITORING INSTRUMENT SYSTEM EMPLOYING A

### GAS CHROMATOGRAPH SENSOR

#### INTRODUCTION

Gas chromatographs have been used in industrial applications for monitoring process streams and controlling the performance of process equipment in refineries and chemical plants for over 18 years. Much of the technology developed for the monitoring control of industrial processes is directly applicable for area monitoring of workplace environments in PVC manufacturing plants. Gas chromatographic monitoring instrument systems similar to the one described here have been installed in a number of industrial applications for monitoring workplace air.

#### GENERALIZED DESCRIPTION OF MONITORING INSTRUMENT SYSTEM

The block diagram in Figure A.16-1 describes the instrument monitoring system used in several of the PVC plants surveyed (refer to Appendices A.1 through A.5).

#### Sample Collection System

Sensor probes are located in work area breathing zones near known potential emission points. In PVC plants, the potential VCM emission points are at seals on reactors, vessels, pumps, compressors and vacuum pumps handling fluids that contain vinyl chloride monomers. The probes are equipped with dust deflecting screen filters and are connected to the sample selector system by means of thin-walled 1/4-inch diameter tubing. The sample selector system transfers the desired sample flow directly to the chromatographic analyzer for analysis. Air is continuously drawn through each probe to assure that a fresh sample is available for each sample point when needed at the sample selector.

#### Chromatographic Analyzer

The chromatographic analyzer has a temperature-controlled oven that contains the sample valves, GC columns, column switching valves, heaters and detector cell. The area outside the oven contains the pressure regulators for gas flow control and the electronics for the temperature control and detector operation. The unit is designed for extended operation without maintenance or manual calibration. The instrument companies selling analyzers equivalent to the Bendix 007 are Beckman, Honeywell, and Process Analyzers, Inc.

#### Chromatograph Programmer

The programmer is designed to operate the valve switching operations within the chromatographic analyzer and the sample selector, and to interface with the output from the detector electronics located in the chromatographic analyzer. The signal output from the programmer is transmitted to a computer and a strip chart

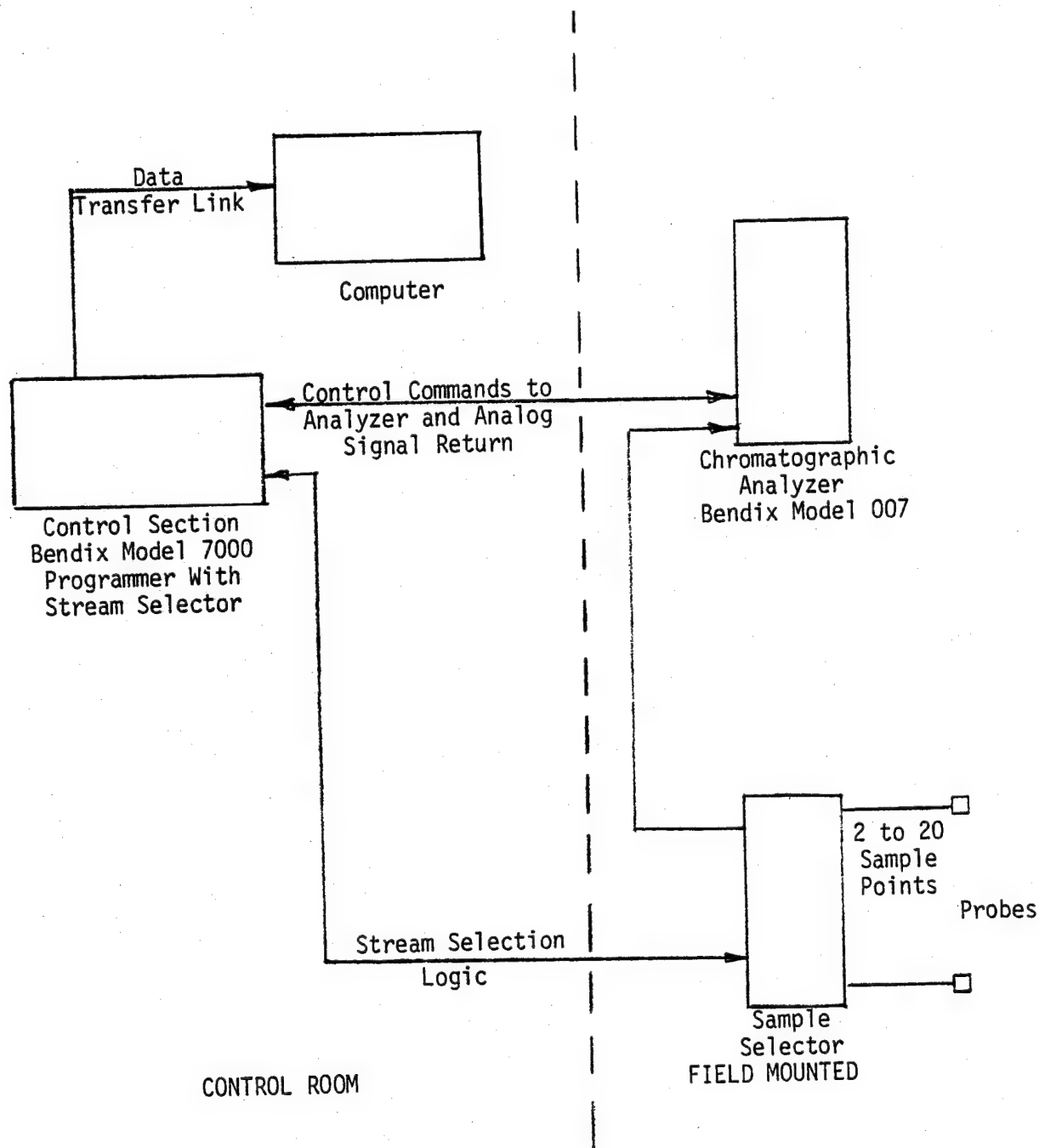


Figure A.16-1. Instrument Monitoring System Employing a Process Gas Chromatograph - Block Diagram

recorder that displays a bar graph readout. Instrument companies that manufacture a programmer equivalent to Bendix Model 7000 are Bechman and Honeywell.

#### Computer Application

Each of the plants employing the gas chromatographic system described here uses their computer in a somewhat different manner. The most sophisticated users also utilized the computer for process control, time and motion study, statistically analyzing various alerts caused by human errors by plant operators, and for printing out data required by federal regulations. The analysis of causes of various alerts gave the plant industrial engineers, the plant industrial hygienists and the plant management a measure of how effective the employee training may be and which employees, if any, may be accident-prone. Also, this analysis of various alerts gave an indication to plant management where to direct engineering talent and capital investment to protect the workers in hazardous environments.

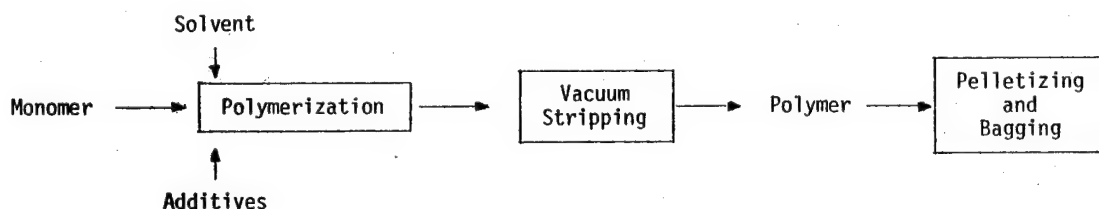
## APPENDIX B. GENERAL FLOW CHARTS AND PROCESS DESCRIPTIONS

### FOR PLASTIC AND RESIN MANUFACTURING\*

The plastic and resin industry is very complex and the following summary describes only the more important processes. The process descriptions are presented in simplified form for each of the 18 process segments. The extremely complex subject of polymer chemistry is not critical to the process segmentation and is not included.

#### BULK POLYMERIZATION PROCESS

Bulk polymerization is the direct conversion of liquid monomer to polymer in a reaction system in which the polymer remains soluble in its own monomer; the reaction is under low pressure.



The reaction is initiated and controlled by catalysts and modifiers. Heat dissipation is a large problem which is overcome by 1) terminating the reaction at a relative low conversion of 40-60% and distilling the excess monomer off, or 2) carrying out the reaction in two steps. In the first step, a large batch of monomer is polymerized to an intermediate conversion and then the reaction is completed in thin layers or in molds to produce a final product. The major benefit of the process is the absence of diluents and impurities in the product.

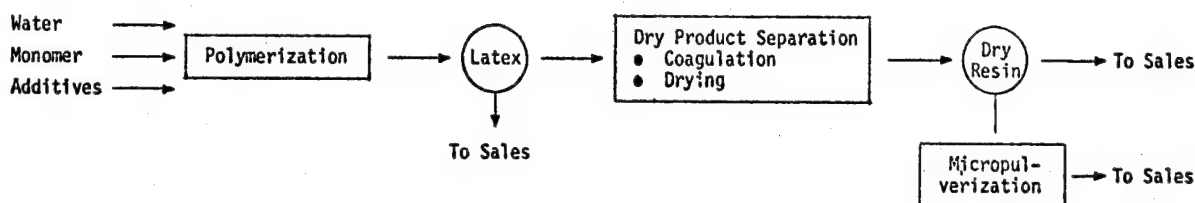
- Typical products: polystyrene, ABS (acrylonitrile-butadiene-styrene), SAN (styrene-acrylonitrile), PVC (polyvinyl chloride), methyl methacrylate, alkyl resins
- Input materials: styrene, acrylonitrile, butadiene, vinyl chloride, methyl acrylate, or alkyl esters of aromatic acids, catalysts, modifiers, solvents

---

\* Environmental Protection Agency. 1976. Industrial Process Profiles for Environmental Use. EPA, Research Triangle Park, North Carolina.

## EMULSION OR DISPERSION POLYMERIZATION PROCESS

Emulsion or dispersion polymerization is characterized by the location of the initiator in the aqueous phase and by the small size of the resin particles produced (10 nm - 1  $\mu$ m). These characterizations also differentiate this process from the suspension process, along with the fact that in dispersion polymerization, the suspended material is liquid.



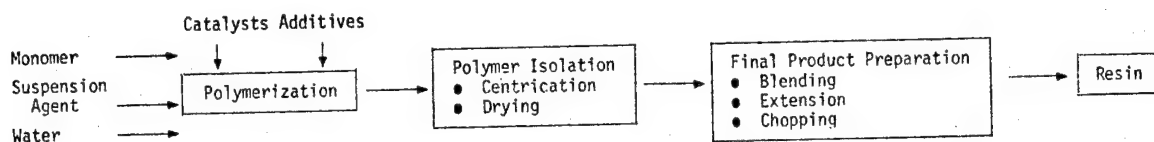
Technical features are the ability to achieve a high rate of polymerization and high molecular weight, low viscosity in the reaction vessel (the polymer being suspended, not dissolved), and the ease of heat dissipation. The operations for producing dry resin are relatively costly and most of the resin is marketed as latex.

- Typical products: (latex) polystyrene, ABS (acrylonitrile-butadiene-styrene), SAN (styrene-acrylonitrile), PVC (polyvinyl chloride), PVA (polyvinyl acetate), polyvinylidene, polyalkyl acrylates and copolymers, polyalkyl methacrylates and copolymers, polyvinyl esters and copolymers, polyacrylonitrile, polybutadiene, polychloroprene, polyisoprene,  $\alpha$ -methylstyrene copolymers, and isobutylene copolymers, nitrile and polyacrylate rubbers, SBR (styrene-butadiene rubber); (dry material) PVC (polyvinyl chloride) plastisol resins, styrene-acrylonitrile graft polyblends with synthetic rubbers, Teflon (polytetrafluoroethylene), Kel-F (polytrifluorochloroethylene).
- Input materials: (monomers) include styrene, acrylonitrile, butadiene, vinyl chloride, tetrafluoroethylene, trifluorochloroethylene, vinyl acetate, alkyl acrylates, alkyl methacrylates, chloroprene, isoprene,  $\alpha$ -methylstyrene, isobutylene; (initiators) usually water soluble peroxide compounds such as hydrogen peroxide, urea peroxide, potassium persulfate, sodium perborate, ammonium peroxydisulfate, cumene hydroperoxide; (emulsifiers) include soaps of long chain alcohols, salts of aliphatic and aromatic sulfonic acids, aliphatic amines and their salts; (modifiers or chain transfer agents) mercaptans, halogenated aliphatic hydrocarbons, or hydrocarbons with an active hydrogen such as cumene; (redox catalysts) water soluble, inorganic reducing agent; commonly, chelated iron; (stabilizers and buffering agents) include casein, glue, albumin, starch, methyl cellulose, polyvinyl alcohol, phosphates, carbonates, etc.; (oxygen scavengers) sodium dithionite, etc.

## SUSPENSION POLYMERIZATION PROCESS

The superficial similarities to emulsion polymerization are exceeded by the technical differences. In this process, finely divided solids or colloids

are used, which do not lower surface tension. The catalyst is soluble in the monomer, and the reaction kinetics approximate those of bulk polymerization. The polymer forms as small spherical particles which are separated, washed, dried and mixed with colorants, etc. and finally extruded and chopped.

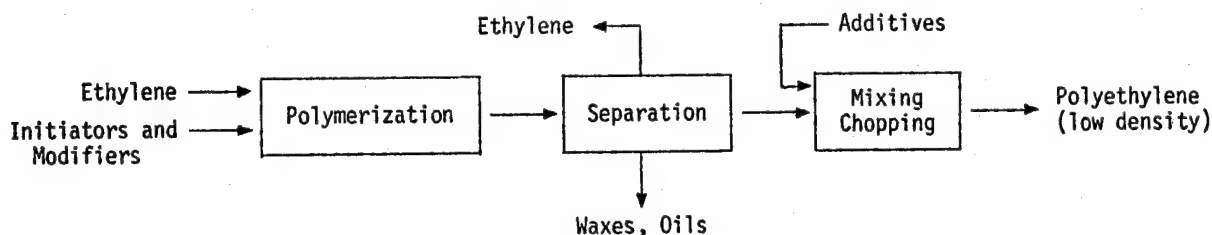


The process enables the recovery of a polymer product of higher purity than the emulsion process in which the coagulation of latex products results in the inclusion of chemical additives. The suspension polymerization product is easily separated from the slurry, washed and dried to form the final dry product. The process also permits good heat transfer and low viscosity.

- Typical products: include polymethacrylic esters and copolymers, polyacrylic esters and copolymers, polystyrene and rubber-modified styrene, polyvinylidene chloride-polyvinyl chloride copolymers, PVC (polyvinyl chloride) and copolymers, PVA (polyvinyl acetate), SAN (styrene-acrylonitrile copolymers), rubber-modified styrene acrylonitrile copolymers, i.e., ABS and others, polydivinylbenzene and copolymers, polychloroethylene and copolymers. Suspension polymerization is the major method for PVC (polyvinyl chloride) production.
- Input materials: (monomers) methacrylic acid esters, acrylic acid esters, styrene, vinylidene chloride, vinyl chloride, vinyl acetate, acrylonitrile, butadiene, divinylbenzene, tetrafluoroethylene, chlorotrifluoroethylene; (suspension agents) (tri)calcium phosphate (hydroxyapatite), barium sulfate, aluminum hydroxide, bentonite clay, calcium oxalate, gelatin, polyvinyl pyrrolidone, polyvinyl alcohol, carboxymethylcellulose, polyacrylic acid, polymethacrylic acid, acrylic-methacrylic acid, ester copolymers; (initiators) include monomer-soluble catalysts, mostly organic peroxides. Also used are benzoyl peroxide, diacylperoxide, lauroyl peroxide, diisopropylperoxydicarbonate, t-butylperoxydibulate; (stabilizers) include polyvinyl alcohol, tragacanth gum, salts of styrene-maleic anhydride copolymers, vinylacetatemaleic anhydride copolymers and salts, starch, gelatin, methylcellulose. Purified (distilled or deionized) water is also required.

#### HIGH PRESSURE BULK POLYMERIZATION PROCESS

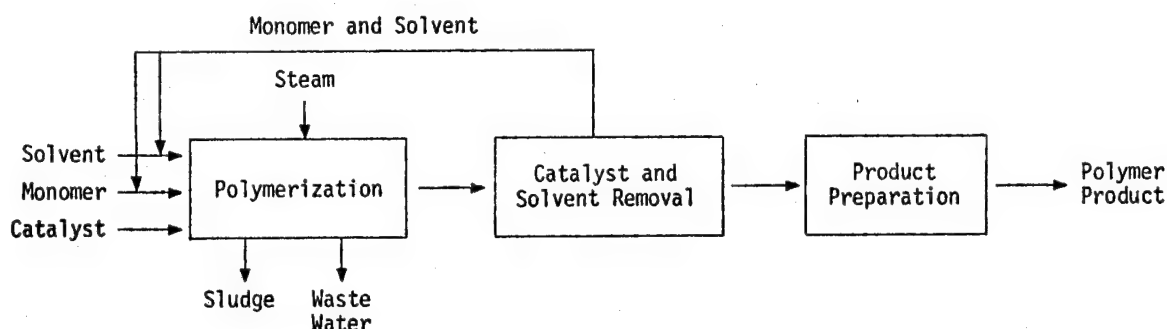
The only major product made through this process is low density polyethylene, one of the most important polymers. Very high pressures are used. The reactor is either tubular or stirred tank, and separation is most commonly in a two-stage separation; there are substantial amounts of ethylene, by-products and solvent to be removed. The polymer may be directly chopped, dried and stored or first treated with colorants, lubricants, etc.



- Typical product: low density polyethylene
- Input materials: (monomer) ethylene; (initiators) air, oxygen, organic peroxides; (chain transfer agents) ketones, aldehydes, alkanes, olefins, alcohols, chlorinated compounds or hydrogen

#### SOLUTION POLYMERIZATION PROCESS

In this process, the monomer, polymer and catalysts are all soluble in the solvent. The solution process favors control of branching and cross-linking but is not widely used because of the cost of solvent recovery, which is done by vacuum drum dryer, falling sheet or strand in vacuum or vacuum extruder.

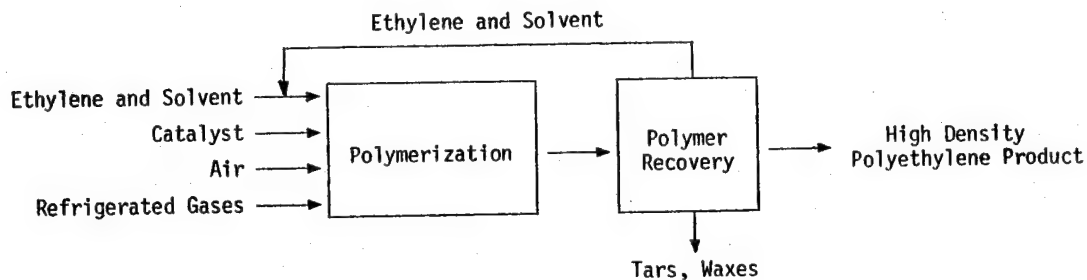


- Typical products: polystyrene, acrylics and ethylene/propylene, butyl and chlorobutyl rubbers, polyisoprene, polysulfide
- Input materials: (monomers) styrene, acrylic acid, methacrylic acid, acrylamide, N-vinyl-2-pyrrolidone, polymerizable vinyl comonomers, isoprene, etc.; (solvents) hydrocarbon solvents used in some systems, water in others. Ethylbenzene is often used in making polystyrene.

#### PARTICLE FORM POLYMERIZATION PROCESS

This process accounts for more production of high density polyethylene than all other processes combined, but ethylene-olefin copolymers are also produced by this process. A distinct similarity to the Ziegler process (Polyolefins Polymerization Process) exists in that both employ a metal catalyst to produce high density polyethylene at low pressures.

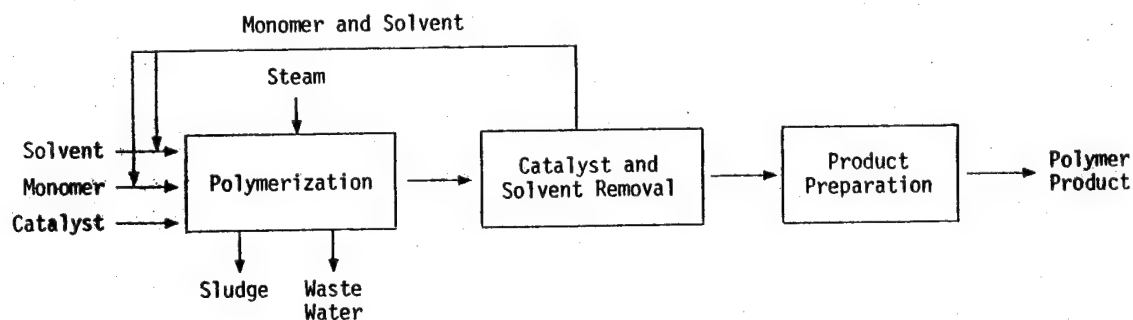




- Typical products: high density polyethylene, ethylene-olefin copolymers
- Input materials: (monomer) ethylene; (solvents) pentane, cyclohexane

#### POLYOLEFINS POLYMERIZATION (ZIEGLER PROCESS)

The use of a metal alkyl or alkyl halide catalyst which is removed from the polymer characterizes the Ziegler process. The process is also unique because the polymer is precipitated as it is formed. The product of the reaction is a slurry of high density polyolefins. There are many process variations in existing plants.

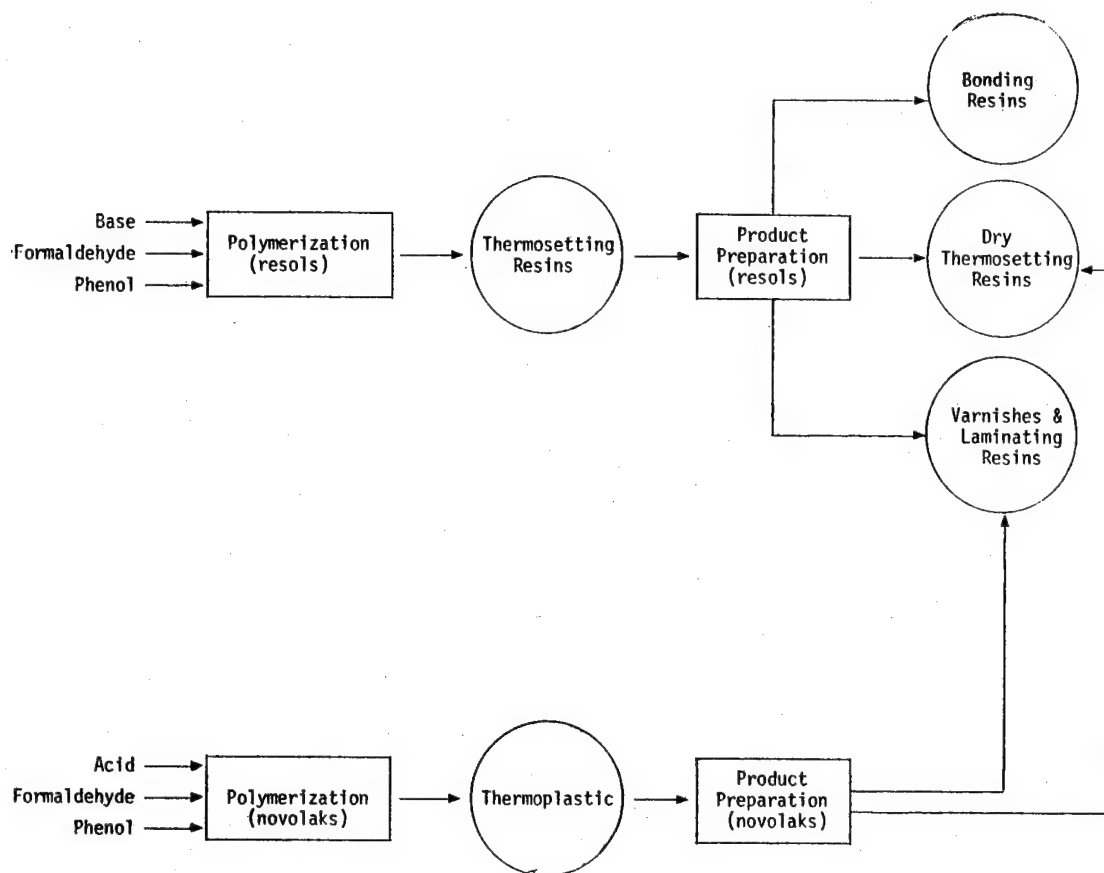


- Typical products: high density polyethylene, polypropylene, various copolymers
- Input materials: catalyst components, hydrocarbon solvents, propylene, butane, ethylene, chain transfer agents (alkyl-zinc compounds, hydrogen)

#### CONDENSATION POLYMERIZATION PROCESSES

##### Phenolic Resin Production Process

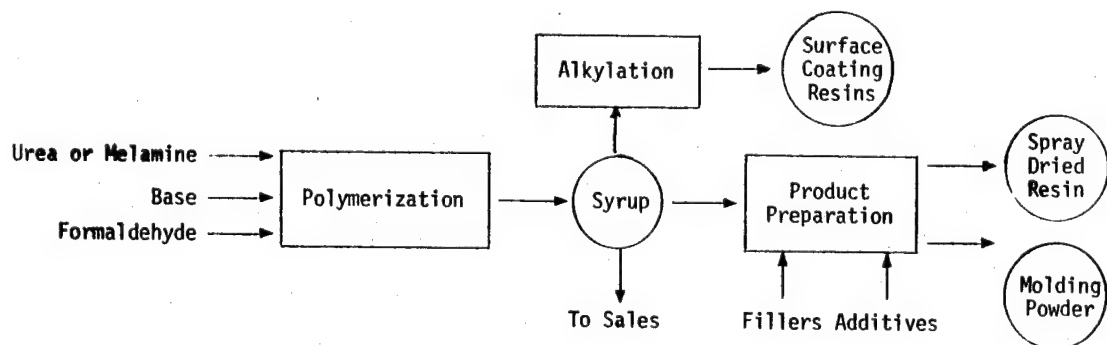
Despite its relative antiquity, the complex reaction process is imperfectly understood. Resols (one-stage resins) and novolaks (two-stage resins) are produced, mainly by batch processes. The resols are formed in an alkaline medium with excess formaldehyde. The excess formaldehyde is in sufficient quantity to complete cross linking and this will occur slowly in storage, if the product is not used within a month or two. The novolak reaction takes place in an acid medium that contains no unreacted aldehyde; the reaction is completed with the aid of added hexamethylenetetramine, etc.



- Typical products: phenolic resins-resols, novolaks
- Input materials: phenol, resorcinol, cresol, formaldehyde, acetaldehyde, hexamethylenetetramine, fillers, pigments, drying oils

#### Amino Resin Production Process

Amino resin production originated with urea-formaldehyde, with malamine becoming the other main amine.

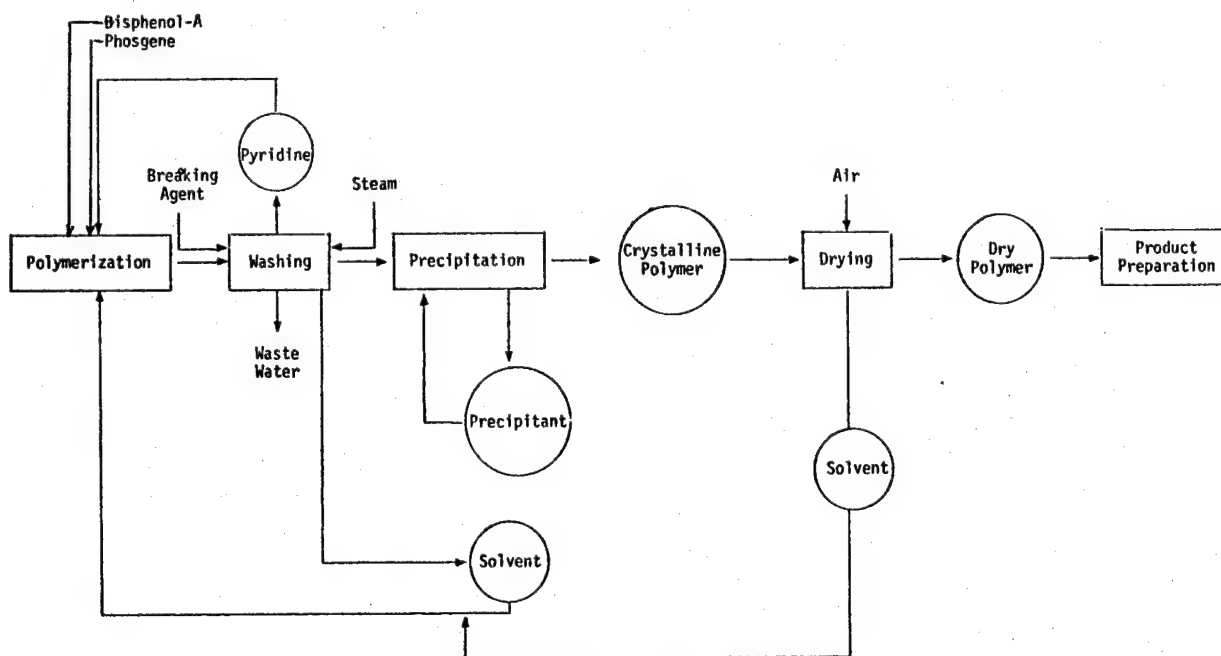


Methylolamines are formed in the first stage in the presence of an acid catalyst by a process similar to that for phenolics. Further polymerization leads to a thick syrupy product which may be shipped as such or dried and combined with pigments and fillers; the syrup has a limited shelf life, but the anhydrous dry solid is almost stable.

- Typical products: urea-formaldehyde, melamine-formaldehyde
- Input materials: urea, formaldehyde, melamine, alkaline compounds, methanol, formic acid, boric acid, benzoquinamine, analines, pigments, fillers

### Polycarbonate Production Process

Polycarbonates are linear thermoplastic polyesters of carbonic acid. The only commercially important polycarbonate is formed by the reaction of bisphenol-A with phosgene in the presence of pyridines. In at least one process, diphenyl carbonate is used rather than phosgene. The polymerization stage in the "pyridine" process has technical advantages, but the pyridine itself and its recovery can be troublesome. Correct proportions of the input and freedom from monohydroxy contaminants are important.

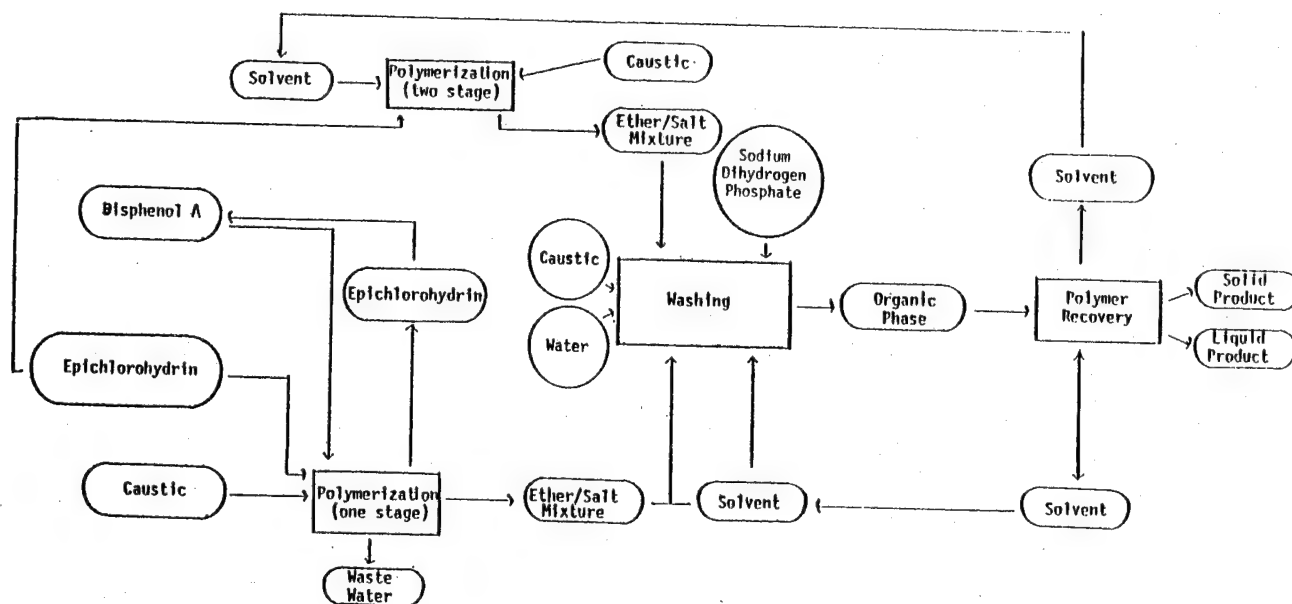


- Typical product: polycarbonate
- Input materials: phosgene, bisphenol-A, pyridine and a solvent such as methylene chloride or chlorobenzene

### Epoxy Production Process

The bulk of the production is unmodified resin, but 10-15% is modified by subsequent reaction with unsaturated fatty acids, etc. The product is either a low molecular weight liquid or high molecular weight solid, produced by

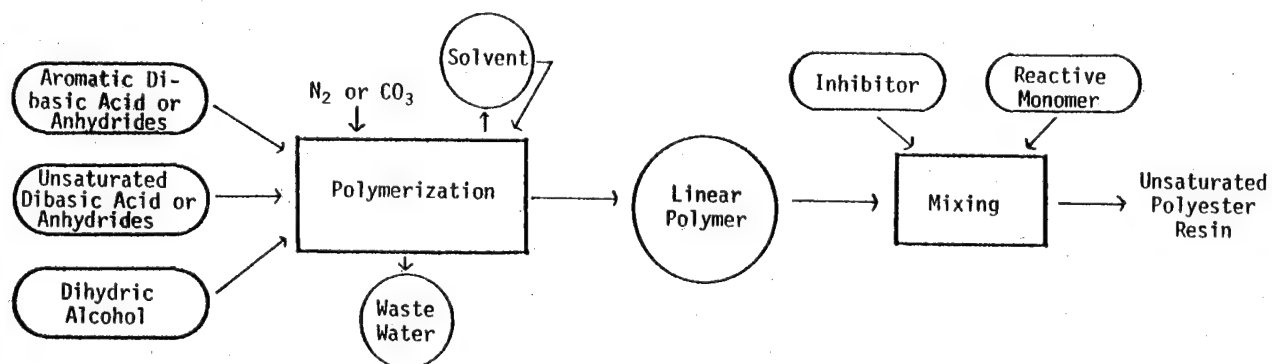
one or two-step polymerization. The epichlorohydrin-bisphenol-A process type exceeds 90% of the total production.



- Typical products: modified and unmodified epoxy resins (liquid or solid)
- Input materials: bisphenol, epichlorohydrin, caustic alkali, cyclopentadiene, other polyolefins, peracids, methyl isobutyl ketone

#### Unsaturated Polyester Resin Production Process

Polyester resins are mixtures of unsaturated polyester resin and vinyl monomers which cross link to form thermosetting resins with the aid of curing agents. The curing operation is performed away from the manufacturing plant, usually at the fabrication point and may require heat and a curing agent.

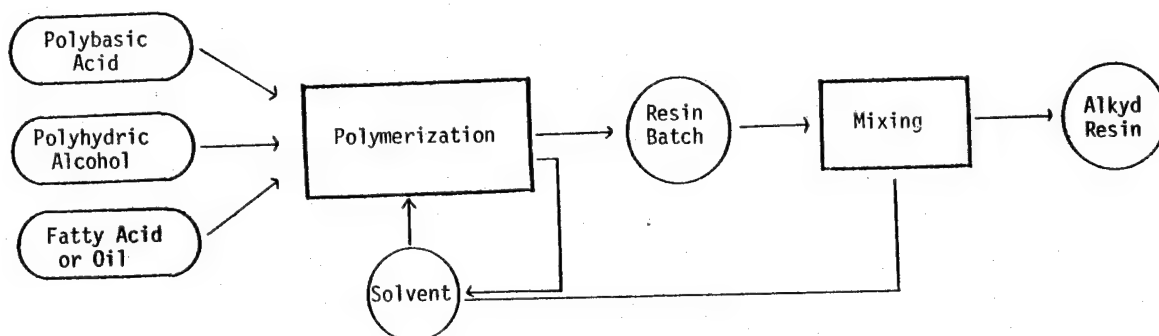


- Typical product: unsaturated polyester resin
- Input materials: The most commonly used unsaturated dibasic acids are maleic, usually in anhydride form, and fumaric acids. The most common aromatic dibasic acid in use is phthalic anhydride, but isophthalic, adipic and azelaic acids are also used. The dihydric alcohol may be ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, etc.

#### Alkyd Resin Production Process

Alkyd resins are actually a specific polyester resin made from polyhydric alcohols, polybasic acids and fatty acids, and produced in hydrocarbon solvent solutions. Much of the alkyd resins produced are ultimately blended with other resins.

The alkyd resins are normally manufactured in the same plant and in the same reactors as the unsaturated polyesters. Basically, only the raw materials and solvents are different between the two resins.



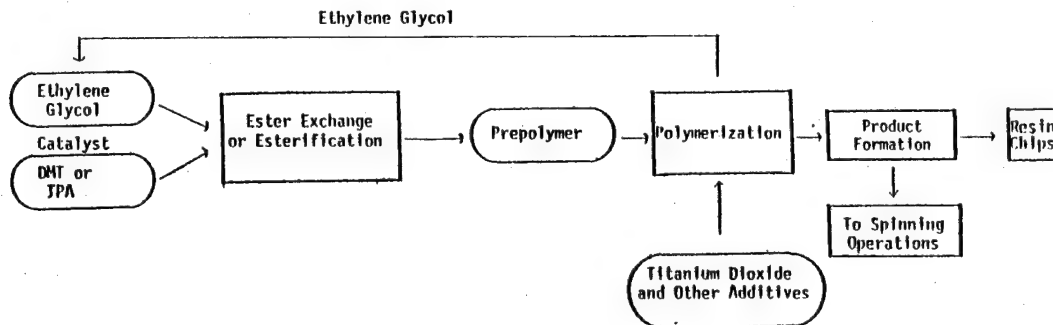
- Typical product: alkyd resin
- Input materials: The polybasic acid is usually phthalic anhydride, although isophthalic acid, adipic acid and sebacic acid are also used. The two most frequent polyhydric alcohols are pentaerythritol and glycerol; others include dipentaerythritol, trimethylolethane, sorbitol, ethylene glycol and propylene glycol. Fatty acids and oils include soya oil, safflower oil, castor oil, linseed oil, coconut oil, cottonseed fatty acids and tall oil fatty acids.

Litharge and lithium are commonly used as catalysts. Solvents are usually xylene or toluene.

#### Polyethylene Terephthalate Production Process

Polyethylene terephthalate is used almost exclusively as feed stock for the synthetic fiber industry. Batch and continuous polymerization processes are

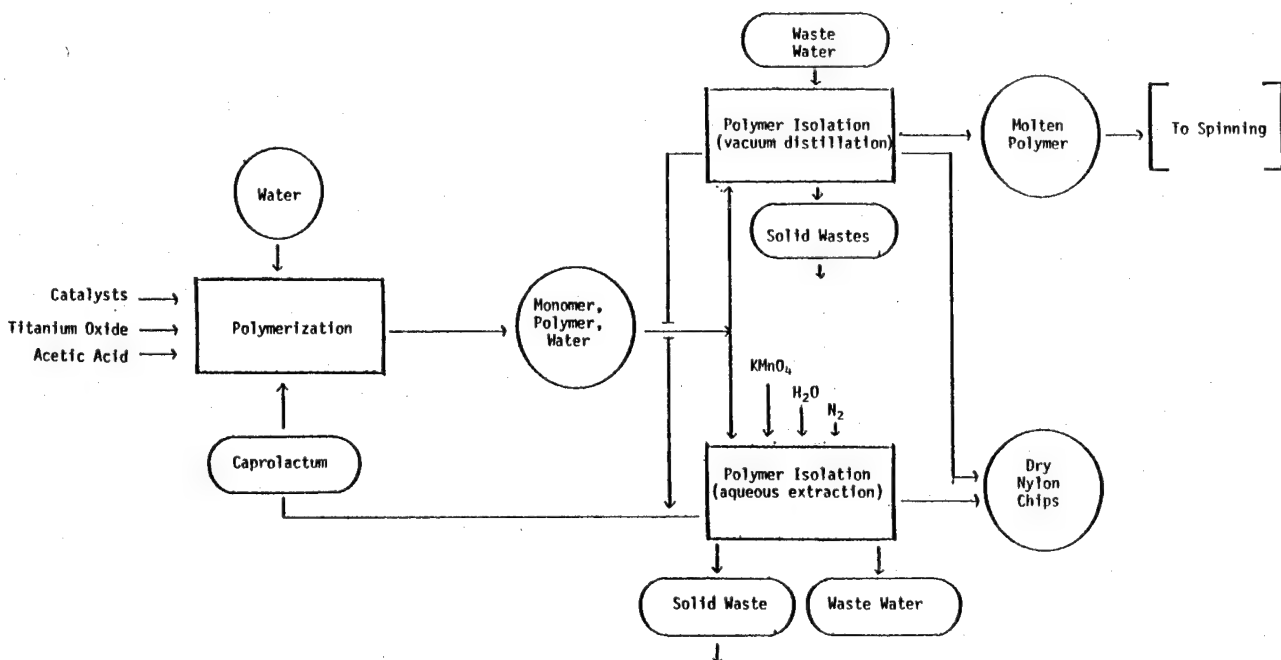
currently in use, although the latter is becoming more important. Terephthalic acid (TPA) has become an alternative to the use of dimethyl terephthalate (DMT), but a large amount of polyethylene terephthalate is still produced by batch process using DMT.



- Typical product: polyethylene terephthalate
- Input materials: ethylene glycol, TPA, DMT, titanium oxide, triaryl phosphites or phosphates, phenolic compounds

#### Nylon 6 Resin Production Process

Nylon 6 is one of several polyamides made by polymerization of an amino acid or a lactam, and is the most important. It is made from caprolactam. Both production methods for Nylon 6 are continuous processes, one using aqueous extraction, the other using vacuum distillation.

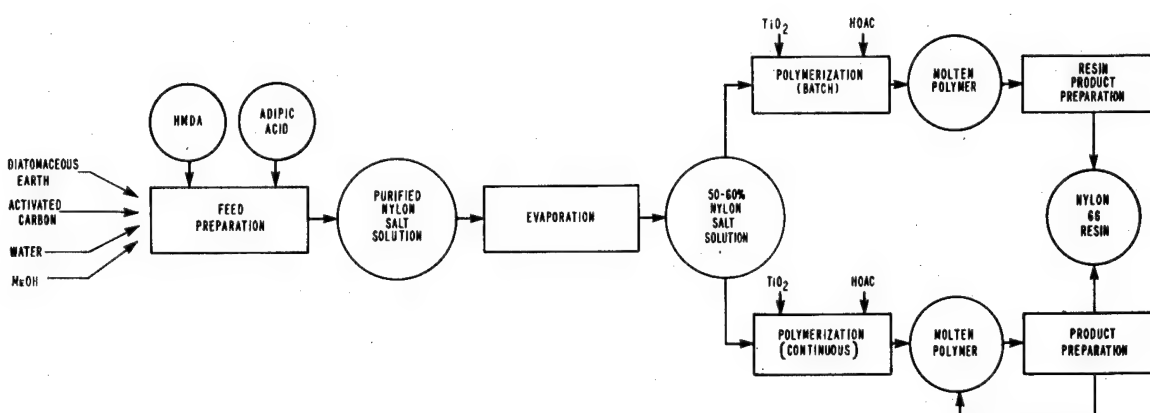


- Typical products: Nylon 6, Nylon 11, Nylon 12
- Input materials: caprolactan, catalysts, water, acidic acid, titanium dioxide, nitrogen, permanganate

### Nylon 66 Resin Production Process

Although other nylons of this type are produced, Nylon 66 is by far the most significant. All are made from reaction of hexamethylene diamine and a dibasic acid (adipic acid is used for Nylon 66).

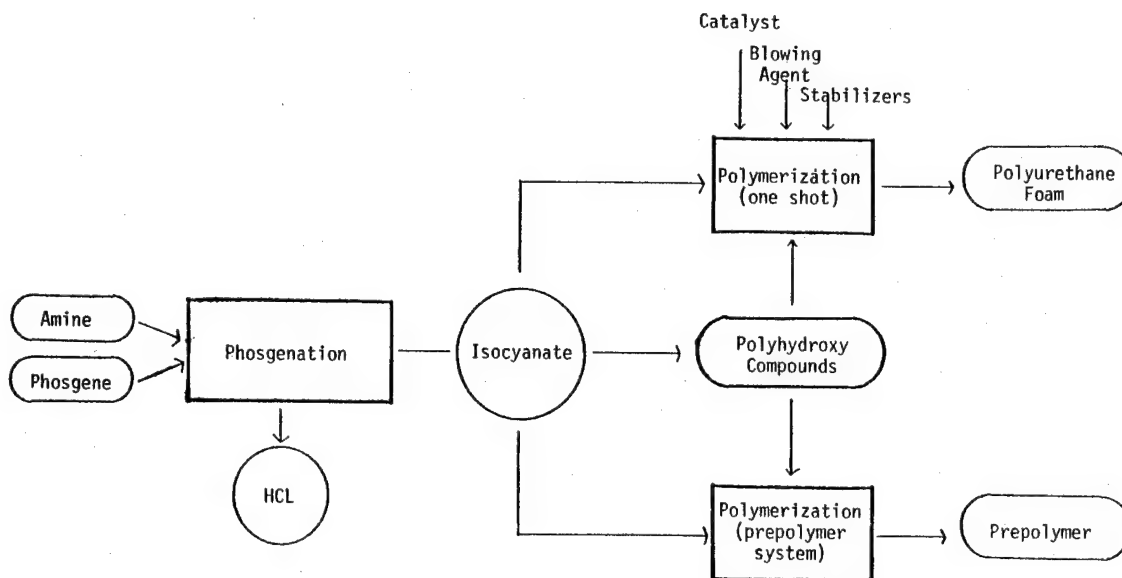
Both batch and continuous processes are used, but most new plants are expected to adopt continuous methods.



- Typical products: Nylon 66, Nylon 610, Nylon 612, Nylon 69
- Input materials: hexamethylene, diamine and adipic acid or hexamethylene diamine adipate, activated charcoal, methanol, acetic acid, titanium dioxide, plasticizers, pigments, etc.

### Polyurethane Foam Production Process

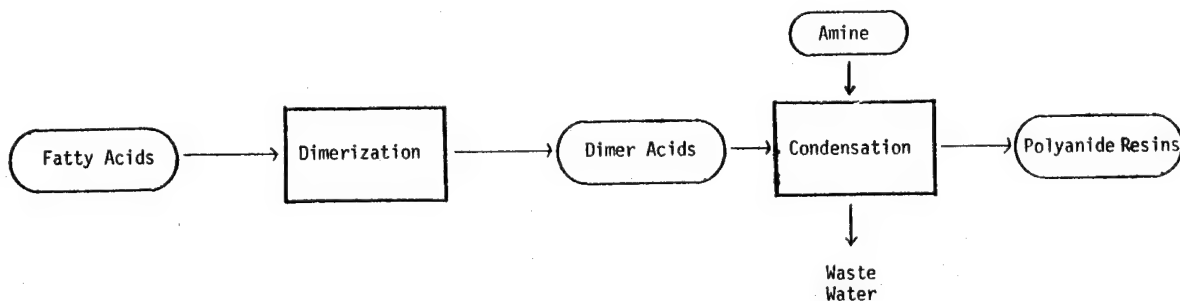
Although the condensation chemistry is complex, it can be regarded basically as a simple condensation of a diisocyanate (two  $-NCO$  groups) and polyol (two  $-OH$  groups), with the elimination of carbon dioxide. The isocyanate manufacture may be at the polymer plant, but a large amount is shipped to users from a few major suppliers. In the one-shot polymerization method, all input materials are combined and the polymerization and foaming are completed. Foaming takes place in foaming devices such as continuous belts for slabs and molds for complex shapes. The prepolymer is cross-linked and foamed later, usually at the location of the purchaser. A continuous processing method may be used, but batch processing is predominant. The prepolymer is formed by reacting an excess of isocyanate with the polyol.



- Typical products: polyurethane foam, polyurethane prepolymer
- Input materials: toluene diamine or diphenylmethane diamine, phosgene, (catalysts) organic tin compounds, tetramethylquinidine, N,N,N',N'-tetramethyl butane diamine, triethylenediamine, dimethylaminoethanol, surfactants, blowing agents, flame retardants (usually liquid organic compounds containing chlorine bromine and/or phosphorus)

#### Polyamide Resin Production Process

The nylon resins are sometimes classed as polyamide resins. The polyamides are either reactive or nonreactive resins based on fatty acids. The resins are generally blended with other resin product.

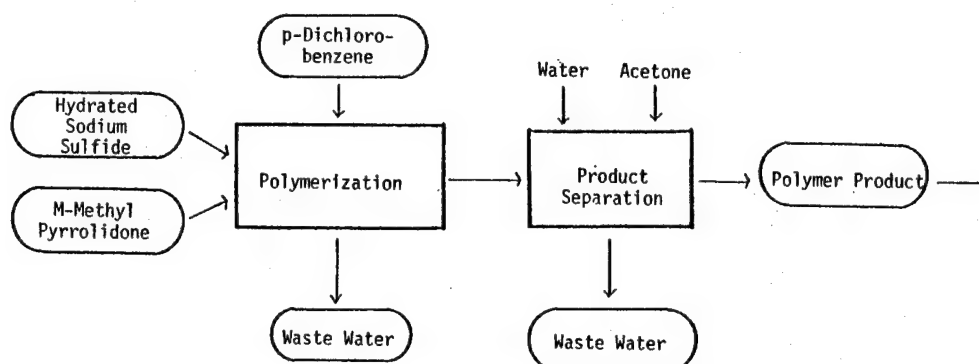


- Typical product: polyamide resin
- Input materials: linoleic and ricinoleic acids, ethylene diamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine



## Polyphenylene Sulfide Production Process

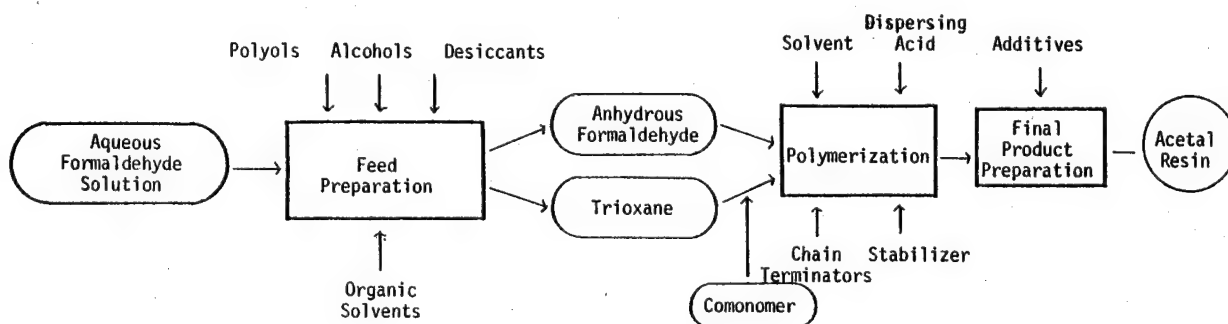
Polyphenylene sulfide has a rigid backbone chain of recurring para-substituted benzene rings. The reaction takes place under heat and, when completed, the crude polymer is dropped into a tank for washing with both water and acetone. The polymer is dried and packaged.



- Typical product: polyphenylene sulfide
- Input materials: p-dichlorobenzene, sodium sulfide, nitrogen, N-methyl pyrrolidone, acetone

## Polyacetal Production Process

Acetal resins are made by addition of aldehyde molecules through the C=O group. Formaldehyde is the aldehyde of principal industrial significance. Both homopolymers and copolymers are produced. The combination formaldehyde and trioxane polymerizations dictate the large number of potential ingredients listed below.



- Typical product: acetal resin
- Input materials: aqueous formaldehyde solution, dehydrating agents, alcohols, nonvolatile polyols, methylene chloride, trichloronaphthalene, trichlorobenzene, propane, cyclohexane, aromatic hydrocarbons, etherified polyethylene glycols, water, methanol, formic acid, acetic anhydride, ethylacetate, benzene, nitrobenzene, methylene dichloride, ethylene dichloride, 1,3-dioxolane, 1,4-dioxolane, ethylene oxide, tetrahydrofuran, amines, phosphines, arsines, stibines, metal carbonyls, metallorganic compounds, sodium acetate, boron trifluoride etherates, aryldiazonium fluoroborates, antimony, trifluoride, iodine, Friedel-Crafts catalysts, perchloric acid, acetyl perchlorate

## APPENDIX C. PROCESS DESCRIPTION FOR COMPOUNDING OPERATIONS

### GENERAL COMPOUNDING

The term "compounding of a polymer" refers to those chemical and, especially, physical methods used to modify the polymer's properties in accordance with specific performance, appearance, or economic requirements. Most commonly, the compounding of a plastic involves the incorporation of certain additives, the compounding ingredients, into the polymer to produce a homogeneous dispersion or mixture. In this way, improvements may be made in processing characteristics (e.g., by the use of plasticizers), in resistance to degradation (e.g., by stabilizers), in strength (e.g., by modifiers or reinforcing fillers), in appearance (e.g., by pigments), by reduction of undesirable characteristics (e.g., by antistatic agents), and by lowering of cost (e.g., by fillers or extenders). Curing agents are also important compounding ingredients, especially in the cases of thermosetting resins and elastomers. The nature and proportions of the compounding ingredients, i.e., the formula or recipe, to be used depends primarily on the nature of the polymer and its intended use.

Important classes of compounding ingredients are antioxidants; antiozonants; antistatic agents; biocides; blowing agents; carbon; catalysts; curing agents; driers and metallic soaps; dyes; inorganic fibers; fillers; flame retardants; pigments; plasticizers; release agents; stabilizers; and, ultraviolet radiation absorbers.

Polymers are modified using a multitude of procedures, but most compounding methods generally consist of three steps (see Figure C-1).

#### Premixing

The premixing or preblending step involves breaking of agglomerates and gross dispersion of compounding ingredients.

#### Fusion

The compounding ingredients are heated and intensively mixed or blended in order to give the polymer particles a homogeneous dispersion on a molecular level.

#### Shaping

The last stage in compounding involves shaping the compounded material into a useable form.

General methods of compounding polymers may be divided into that of compounding thermoplastics and that of compounding thermosetting resins. This is

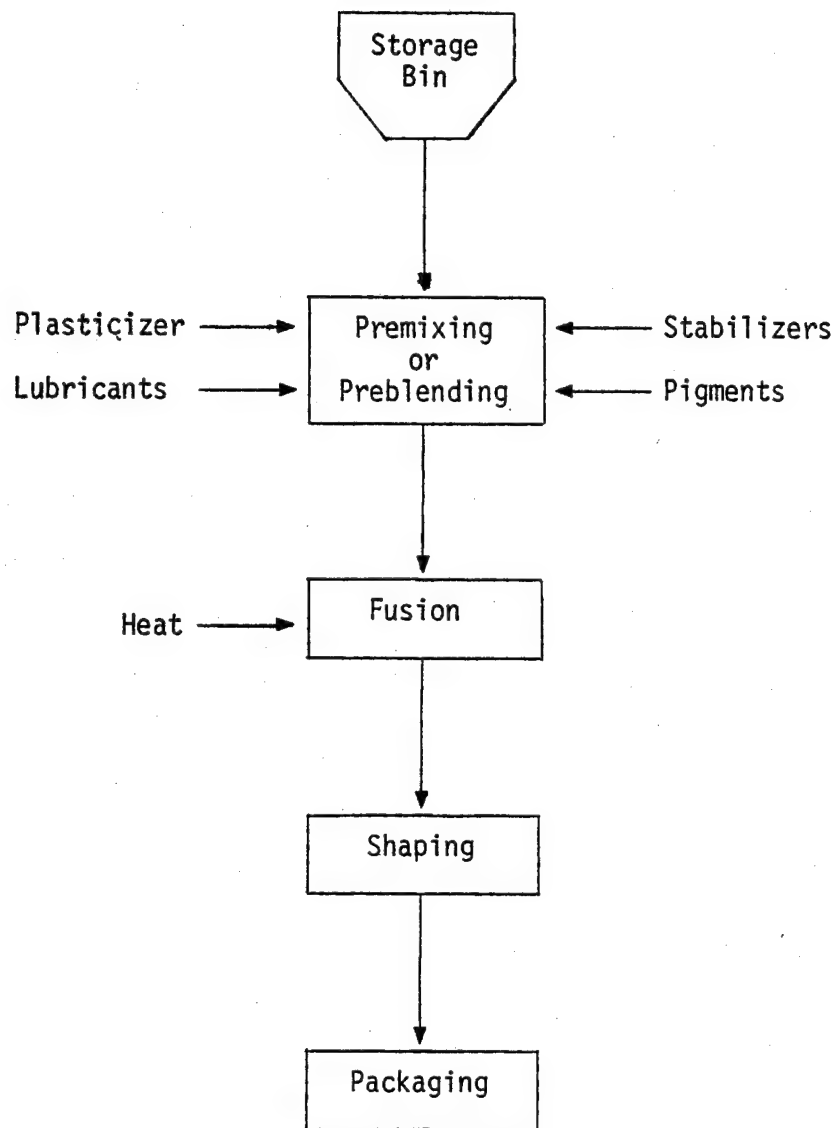


Figure C-1. Compounding Process Flow Diagram

because the effect of heat differs greatly depending whether the polymer is the former or the latter. The compounding of elastomers is a specialized technology. This appendix will describe the general methods of compounding thermoplastic polymers and the specialized technology of compounding elastomers.

## COMPOUNDING OF THERMOPLASTIC POLYMERS

### Premixing

Preblending involves the breaking up of thermoplastic aggregates, devolatilization and the gross mixing of the compounding ingredients. The usual compounding materials added to thermoplastics are various agents to protect the polymer during processing and use from degradation caused by heat, light, oxygen, or microorganisms. In addition to these materials which are present usually in small amounts (less than 3 parts per hundred, phr), colorants, fillers and plasticizers are important materials which are present in larger amounts (up to about 300 phr in highly filled materials). The order of addition depends largely on the nature of the various materials involved and no generalizations may be made. However, it is an important factor since the mixture must be kept as fluid as possible throughout the compounding operation.

The premixing operations may be carried out in large batches with the aid of mixers and blenders. In mixing dry materials (e.g., in dry coloring), a less intensive type mixer, like ribbon blenders, conical mixers or sigma-blade blenders may be used. If the material is dough- or taffy-like, a more intensive mixer, like the Muller-type mixer, or vortical-action mixer will be required (as in the mixing of color concentrates with uncolored resin).

The premixed materials are usually screened to eliminate remaining aggregates before the next operation.

### Fusion

The second step in compounding thermoplastics involves fusion by the external application of heat, shearing action, or both. The compounding ingredients are thereby allowed to penetrate into what was the inside of the (now molten) polymer particles to give a homogeneous dispersion on the molecular level.

A number of different types of equipment are available for this purpose. Extruders are widely used. They provide heating by shear and permit continuous operation.

The Banbury internal mixer is particularly useful for compounding plastics that are difficult to process and for compounding and reclaiming elastomers. It is usually employed in conjunction with a two-roll mill or an extruder.

### Shaping

The last stage in compounding a thermoplastic involves shaping of the compounded material into useable form. For example, the Banbury mixer will produce thick, shapeless masses of several hundred pounds that must then be cut into small pieces. The compounded material is therefore placed on a

two-roll mill and a sheetlike material is produced. The sheet can be reduced in size by cutting and further subdividing into granules or pounds.

The product from an extruder can be obtained in tape, tube or strand form as final product or, after cooling, may be granulated. Pellets can be obtained directly by die-face cutting, whereby the extruded polymer is cut under water while still hot upon emerging from the extruder.

## COMPOUNDING OF THERMOSETTING POLYMERS

### Premixing

Thermosetting resins are usually in the form of a syrup or of a finely divided powder prior to compounding. They are mixed with a variety of other solids, e.g., fillers like wood flour, asbestos, clay or mica. In addition to the usual compounding ingredients, thermosetting resins are also compounded with suitable curing agents. This is carried out at a stage at which they are still not fully set.

Equipment used for compounding includes ball mills, sigma-blade blenders and vortical mixers. Ball milling is particularly useful for the production of powders with exact shades of color.

### Fusion

The sensitivity of resins to heatsetting must be taken into account. Heating can be only carried out at low temperatures and for short periods of time. Likewise, pH conditions must be carefully controlled.

Fusion (fluxing) for brief periods can be performed on two-roll mills or a Banbury mixer.

### Shaping

The compounded material produced from the two-roll mills or Banbury mixer may be then reground into a powder or granulated after extrusion.

## NATURAL RUBBER AND SYNTHETIC ELASTOMER COMPOUNDING

### Premixing

High quality natural rubber is too hard and tough to process well. Therefore, the first step in its use is a preliminary breakdown or mastication. This is accomplished by the shearing action of a two-roll rubber mill, or an internal mixer such as a Gordon plasticator. This breakdown causes the rubber to become smoother, more plastic and more thermoplastic in subsequent steps.

Most synthetic elastomers also require some breakdown of a similar type. The amount required varies with the type and grade of elastomer under consideration. In most cases, the breakdown of synthetic elastomers differs from and is less extensive than that of natural rubber.

All rubber compounds contain some added chemicals and most of them contain softeners and pigments. All of these materials must be thoroughly blended

with the rubber to give an essentially homogeneous mixture.

When using an internal mixer of the Banbury type, the rubber is added first and then worked. The compounding ingredients are added later and worked in. Many types of elastomers, such as those for tire treads, are mixed in several steps.

### Fusion

The premixing is followed by charts of power consumption and temperature. Heat is developed by the mechanical working during mixing. On a molecular level, the polymer chain molecules are broken down either mechanically or by oxidation. At temperatures below 65°C, the rupture of the molecules is largely mechanical, leaving free radicals, which react either with the oxygen from the air or with some radical acceptor in the compound. The shearing force decreases rapidly up to temperatures of 100°-120°C because of the thermoplasticity of the rubber. This is the range of minimum permanent breakdown of natural rubber.

This step is carried out usually by the same mixers in the premixing step. In many cases, especially when mixing in a high-speed mixer, the temperature rise in the batch is quite rapid. To prevent scorching or premature vulcanization part or all of the curing agents may be kept out of the batch until the final mix. The batch is dumped onto a sheeting mill as soon as it reaches a definite temperature instead of being mixed for a definite period of time. The batch comes out of the Banbury mixer in chunks of various sizes which are dropped on to a two-roll mill under the mixer. On this mill, the batch is further blended, sheeted and cooled. It is cut off the mill in sheets, cooled in water, dusted or dispersed with separators to prevent sticking and stored for further processing.

### Shaping

There is a wide variety of ways to shape rubber products. A widely used method either as an intermediate or end product is extrusion through a tuber or extruder. Calendering, another method, produces a smooth, uniform sheet of unvulcanized rubber by pressing between rollers. Such sheets may be cured as sheeting, cut into threads, or plied with fabric. In a friction calender, the rubber stock is pressed and smeared into the interstices of woven fabric to make raincoats, boots, etc. Another method is to spread or coat properly compounded latex or cements onto fabrics. The machines required for spreading and coating are simpler and cheaper than those used for calendering, but the coated fabrics must be dried. When cords are used instead of fabrics, they are usually dipped into latex and then dried. Vulcanization and curing are also undertaken, but these are fabrication questions and do not fall under the scope of this study.

#### APPENDIX D. HEALTH EFFECTS

Since there are so many different chemicals used in the plastics and resins industry, it is not practical to expound on the toxicological properties of each. However, a brief summary of the adverse health effects associated with each of the major raw materials is presented along with any existing federal exposure limits.

##### Acrylamide (Propeneamide)

Acrylamide is a vinyl monomeric powder (MP 84.5°C) used in the preparation of special polymers.

The absorption of acrylamide through the skin or by dust inhalation has been shown to cause serious neurological reactions. The variable polyneuropathy is characterized by numbness, weakness, ataxia, tremor and dysarthria. Although recovery over several months is usual in mild intoxications, severe intoxications cause permanent neurological damage consistent with mid-brain lesions.

The current OSHA 8-hour TWA for acrylamide is 0.3 mg/m<sup>3</sup>.

##### Acrylic Acid Derivatives (Methyl and Ethyl Acrylate)

Both are colorless liquids (methyl, BP 80°C; ethyl BP 99°C) which polymerize readily and very exothermically at room temperatures, and are therefore shipped and stored with inhibitors added. They are polymerized to macromolecules with film-forming properties which are used to make paints, coatings and adhesives.

These acrylates are extremely irritating to the whole respiratory tract; on acute exposure, respiration becomes rapid, the lips cyanotic and convulsions may occur. Death occurs as a result of pulmonary edema. If they are splashed in the eye, severe burns and opacity of the cornea result. Prolonged skin contact leads to severe irritation and systemic poisoning due to adsorption. Animal tests have shown liver and kidney damage following cutaneous absorption.

Methyl acrylate can be detected by smell at 20 ppm and ethyl acrylate at 8 ppm.

##### Acrylonitrile (Vinyl cyanide)

Acrylonitrile is a colorless or slightly yellow liquid with a very faint odor (BP 77.3°C) which is polymerized to produce synthetic fibers (orlon, acrylon) or copolymerized with butadiene to make nitrile rubber.



Acrylonitrile is a poisonous liquid both when its vapors are inhaled and when liquid or vapor is absorbed by the skin. Acute poisoning is characterized by nausea, headaches, deafness, sneezing, exhaustion, abdominal pains and vomiting; on prolonged exposure, loss of consciousness, asphyxia and death. Subacute poisoning shows milder symptoms; mainly, tiredness and loss of appetite. Subacute poisoning has been demonstrated with doses of 16-100 ppm in air for 20-45 minutes.

The OSHA 8-hour TWA standard for acrylonitrile is 20 ppm (45 mg/m<sup>3</sup>). Recent animal and epidemiological studies indicate acrylonitrile may be a cause of cancer in humans. OSHA is considering a new standard which will regulate acrylonitrile as a human carcinogen.

### Aniline

Aniline is an oily liquid (BP 184.4°C) with a strong amine-like odor which is used to manufacture thermosetting resins by condensation with formaldehyde.

Aniline is very toxic when breathed or absorbed through the skin; its toxic action is directed on the blood and central nervous system. In acute poisoning, cyanosis is seen, especially in the nose, lips and nails due to the formation of methemoglobin. The central nervous system is first excited, with manifestations of euphoria, exaggerated reflexes, and accelerated breathing, soon followed by generalized weakness and drowsiness.

Aniline can have a necrotizing effect on the cornea and can also produce acute eczematous lesions on contact with the skin.

The OSHA 8-hour TWA standard for aniline is 5 ppm (19 mg/m<sup>3</sup>).

### Benzene

Benzene (C<sub>6</sub>H<sub>6</sub>) is a clean, colorless, non-corrosive, highly flammable liquid with a strong, pleasant odor. Benzene's low boiling point and high vapor pressure causes it to evaporate rapidly under ordinary atmospheric conditions giving off vapors nearly three times heavier than air.

Due to its volubility, the major route of entry of benzene is by vapor inhalation. In acute exposures, benzene toxicity appears to be due primarily to its effect on the central nervous system.

The benzene absorbed by the circulating blood is distributed throughout the body where, because of its liposolubility, it tends to accumulate in various body organs in proportion to their fat content.

OSHA issued an emergency temporary standard for benzene to limit employee exposure to airborne concentrations of benzene to 1 ppm as an 8-hour time-weighted average.

### Butadiene (1, 3-Butadiene)

Butadiene is a colorless gas (BP-4.7°C) with a slightly aromatic odor. It is

used in the production of synthetic rubber by a process of polymerization with some other monomeric components such as styrene or acrylonitrile.

Butadiene shows low toxicity when inhaled in concentrations up to 8000 ppm; at such concentrations there are complaints of cough, nasal mucosal congestion, eye irritation and drowsiness. Recovery is rapid and complete, as butadiene is not retained in the body. At very high concentrations, butadiene shows anaesthetic and narcotic effects.

The OSHA 8-hour TWA standard for butadiene is 1000 ppm (2200 mg/m<sup>3</sup>).

#### Caprolactam (Cyclohexanone Iso-Oxime)

Caprolactam is a water-soluble solid (MP 69°C) which is used in the manufacture of homogeneous linear polyamides (polycaprolactams) and synthetic fibers (perlon).

Due to its low volatility, caprolactam does not present a serious hazard of acute poisoning. Average air levels of caprolactam in a polymerization shop and weaving workshops were reported to be 20-40 mg/m<sup>3</sup>. In spinning shops where workers complained of irritability and nervousness, investigators found concentrations of 60 mg/m<sup>3</sup>.

No OSHA standard for caprolactam has been established.

#### Chloroprene (2-Chlorobutadiene)

Chloroprene is a slightly colored liquid (BP 59.4°C) which is used in the production of elastomers such as neoprene and isoprene.

Chloroprene vapors cause mucous membrane inflammation and edema of the eyelids. Toxic effects on the respiratory system, liver, kidneys (bile pigments and albumen in the urine) and circulatory system (arterial hypotension) have been observed at a dose of 83 ppm in air. Loss of appetite and indigestion are also observed. Chloroprene is readily absorbed through the skin and can cause both acute and chronic poisoning via this route.

The OSHA 8-hour TWA standard for chloroprene is 25 ppm (90 mg/m<sup>3</sup>).

NIOSH has recommended 1 ppm, 15-minute ceiling exposure to chloroprene.

#### Chlorosilanes (Silicone Intermediates)

Silicone tetrachloride and methyl and ethyl chlorosilanes are colorless liquids used in the manufacture of silicones.

These chemicals are highly toxic and caustic, causing burns and irritation of mucous membranes, if splashed onto the skin or inhaled in vapor form.

No OSHA 8-hour TWA standard has been established.

### Epichlorohydrin (1-Chloro-2, 3-Epoxypropane)

Glycerol epichlorohydrin is a colorless liquid (BP 116°C) with an irritating odor of chloroform. It is used to make epoxide resin by condensation with diphenols, especially propane.

Epichlorohydrin vapors irritate the mucous membranes; 20 ppm will cause burning of eyes and mucosa within an hour. Acute poisoning can result in pulmonary edema and kidney damage. Low concentrations can cause chronic poisoning with fatigue, gastrointestinal pains, chronic conjunctivitis and coryza. If the liquid is splashed in the face, it can cause opacity and necrosis of the cornea.

The OSHA 8-hour TWA standard for epichlorohydrin is 5 ppm (20 mg/m<sup>3</sup>).

NIOSH has recommended a TWA exposure limit of 0.5 ppm (2 mg/m<sup>3</sup>).

### Ethylene

Ethylene is a colorless gas (BP 103°C) which is used to produce polyethylene plastic.

Ethylene is a fairly nontoxic gas which is occasionally used as a surgical anesthetic. The greatest hazard which the handling of ethylene presents is its wide explosive range in air.

There is no current OSHA 8-hour TWA for ethylene.

### Ethyleneimine

Ethyleneimine is a colorless oily liquid (BP 55°C) with a strong ammonia odor which is polymerized to give the thermoplastic polyethyleneimines.

Ethyleneimine is highly toxic to man both by inhalation of vapors and by absorption through the skin. Breathing vapors cause nausea and vomiting as well as a characteristic swelling of the eyelids, mouth and throat. Liquid ethyleneimine readily penetrates intact skin to cause systemic poisoning as well as irritation and necrosis at the site of contact. The ethyleneimine radical is carcinogenic but can also show anticarcinogenic effects such as growth inhibition, arrest of mitosis, etc.

The OSHA 8-hour TWA standard for ethyleneimine is 0.5 ppm (1 mg/m<sup>3</sup>).

### Formaldehyde

Formaldehyde is a colorless gas (BP -19.5°C) with a strong irritating odor. It is usually supplied in a 30-55% aqueous solution with 6-15% methanol added as a stabilizer. Formaldehyde is used in the plastics and resins industry to make thermosetting resins such as phenol-formaldehyde resins, urea-formaldehyde resins and others.

The major toxic effects of formaldehyde vapor are acute respiratory and eye

irritations which become chronic on continued exposure to low concentrations (10-30 ppm). Concentrated solutions of formaldehyde can cause necrosis of the skin, while dilute solutions cause an eczematoid dermatitis.

The OSHA 8-hour TWA standard for formaldehyde is 3 ppm (3.6 mg/m<sup>3</sup>).

NIOSH has recommended a 1 ppm (1-2 mg/m<sup>3</sup>) 30-minute ceiling for formaldehyde.

Paraformaldehyde is a solid polymer of formaldehyde, which depolymerizes rapidly upon heating. It is combustible and has the strong odor of formaldehyde. Contact of the solid material with the skin or mucosa will cause the same type of symptoms as formaldehyde exposure. There is no OSHA permissible exposure limit for paraformaldehyde.

### Furfural

Furfural is a light yellow liquid (BP 161.7°C) which is used in the plastics and resins industry to make phenol-furfural thermosetting resins.

Furfural is a toxic liquid whose vapors are very irritating to mucous membranes, especially those of the eye. In sufficiently high doses, it is a central nervous system poison.

The OSHA 8-hour TWA standard for furfural is 5 ppm (20 mg/m<sup>3</sup>).

### Organic Isocyanates

There are many isocyanates, but the most important commercially are:

- Toluene 2, 4- and 2, 6-diisocyanates
- Toluene 2, 4-diisocyanate dimer
- Methylene bisphenyl isocyanate
- 4, 4', 4'' - triphenylmethane triisocyanate

Some are liquids with high vapor pressure while some are solids sold in solution with chlorobenzene, ethyl acetate, or methylene chloride. Isocyanates are reacted with polyols or polyesters to give polyurethanes. These polymers are used as elastomers, cellular materials and resins used in coatings and adhesives.

Acute toxic reactions to toluene diisocyanate vapors include acute bronchitis and, at high concentrations, pulmonary edema; in the eye, the vapor causes lachrymation and burns to the mucosa of the eye. Chronic exposure to small quantities of the vapor causes chronic irritation of the mucous membrane of the eyes and upper respiratory tract which may be accompanied by bronchospasm, causing considerable difficulty in breathing. Short-term exposure to high levels of the vapor may result in sensitization to trace concentration levels.

The OSHA 8-hour TWA standards for isocyanates are toluene-2, 4-diisocyanate, 0.02 ppm (0.14 mg/m<sup>3</sup>); methylene bisphenyl isocyanate, 0.02 ppm (0.2 mg/m<sup>3</sup>).

NIOSH has recommended a 0.005 ppm TWA for toluene-2, 4-diisocyanate.

### Hexamethylenediamine (1, 6-Diaminohexane)

Hexamethylenediamine is a colorless powder (MP 39<sup>0</sup> - 42<sup>0</sup>C) which is usually shipped and stored in solution; it is used to make nylon-66 by condensation with adipic acid.

Aqueous hexamethylenediamine is caustic, irritates the skin, ocular mucous membrane and respiratory tract. The chemical also has systemic toxic effects which include hemolytic anemia and leucopenia.

OSHA has not set an 8-hour TWA standard for hexamethylenediamine.

### Methacrylonitrile

Methacrylonitrile is a liquid (BP 90.4<sup>0</sup>C) which is polymerized to give polymethacrylonitrile plastics.

Methacrylonitrile shows toxicity very similar to acrylonitrile, the only differences being that methacrylonitrile is more readily absorbed through the skin and causes less irritation to skin and mucous membranes. Due to its lower vapor pressure, methacrylonitrile probably does not present as great an inhalation hazard as acrylonitrile.

No OSHA TWA standard has been established for methacrylonitrile.

### Methyl Methacrylate

Methyl methacrylate is a colorless liquid (BP 100<sup>0</sup>C) with a sweet characteristic odor, which is polymerized to polymethyl methacrylate (Plexiglass, Lucite, etc.), a very important plastic commercially.

The toxicity of methyl methacrylate is much less than either of the two acrylates mentioned above. It is a mild irritant to respiratory mucous membranes and can cause a dermatosis.

The OSHA 8-hour TWA standard for methyl methacrylate is 100 ppm (410 mg/m<sup>3</sup>).

### Phenol

Phenol is a crystalline solid which, in the anhydrous state, melts at 43<sup>0</sup>C. Phenol is used widely in the manufacturing of phenol-formaldehyde thermosetting resins, caprolactam, certain polyamides and polyurethanes, and in making plasticizers such as triphenyl phosphate and phenol-cresol alkyl sulphonate.

Acute toxic reactions to phenol inhaled or absorbed through the skin include paralysis due to central nervous system poisoning, and edema of lungs, kidneys, liver and spleen. Dermal exposure to the crystals, liquid, or aqueous solutions causes marked irritation and caustic action.

Chronic toxicity can occur if there are repeated exposures to low concentrations of phenol over long periods of time. Systemic symptoms include digestive disturbances, loss of appetite, copious salivation, headaches and vertigo.

The liver and kidneys may be affected. Chronic dermal exposure may result in gangrenous lesions which develop rapidly from apparently benign lesions.

The OSHA 8-hour TWA standard for phenol is 5 ppm (19 mg/m<sup>3</sup>).

### Propylene

Propylene, like ethylene, is a colorless gas (BP 48°C) used in the manufacture of polypropylene plastics.

Propylene is fairly nontoxic, although flammable, and no OSHA 8-hour TWA has been set for it.

### Polymer Additives

The most important polymer additives will be listed below with brief descriptions of their toxic properties.

- Phthalate esters (plasticizers): very low toxicity for man
- Phosphate esters (flame retardant): pure compounds, nontoxic; may be contaminated with orthotricresyl phosphate, a potent neurotoxin
- Chlorinated biphenyls (plasticizers): associated with toxic effects on the liver and dermatitis (chloracne)
- Organic peroxides (curing agents): strong oxidizing agents which can cause skin irritation or burns and severe eye damage
- Elastomer vulcanizing agents: the following compounds are added to elastomer polymer systems to accelerate vulcanizations:

Benzothiazolyl disulfide  
Mercaptobenzothiazole (MBT)  
Tetraethyl thiuram disulfide (disulfiram)  
Tetramethyl thiuram disulfide (thiram)  
Thiocarbanilide  
Dithiocarbamates  
Diphenylguanidine phthalate  
Hexamethylene tetramine

Absorption of disulfiram or thiram by any route produces severe reactions when alcohol or paraldehyde is subsequently consumed. These reactions include flushing, palpitations, dyspnea, nausea and hypotension.

- Antioxidants: the following additives are used to halt the degradation of rubbers by atmospheric oxygen:

Monobenzylether of hydroquinone  
S-di-(B-naphthyl)-P-phenylenediamine  
Mono and dioctyl diphenylamines  
Phenyl naphthylamine

The monobenzyl ether of hydroquinone can cause loss of skin pigment without previous sensitization. Most of the amines are potent sensitizers, causing delayed allergic reactions.

### Styrene (Vinylbenzenephenylethylene)

Styrene is a colorless liquid (BP 145.2°C) with a characteristic odor which is used in the production of polystyrene, or copolymerized to produce synthetic rubbers and many different polyesters.

Air concentrations of styrene in the range of 400-700 ppm cause symptoms of irritation of eyes, mucous membrane, and upper respiratory tract as well as nausea and loss of appetite. At concentrations above 1300 ppm, styrene can cause lesions to upper respiratory tract and other mucosa; 10,000 ppm can be fatal in 30-60 minutes. Prolonged skin contact causes dryness and strong irritation.

The OSHA TWA standard for styrene is 100 ppm (420 mg/m<sup>3</sup>).

### Vinyl Acetate

Vinyl acetate is a colorless liquid (BP 72.7°C) with a sweet odor. Since it polymerizes spontaneously at room temperature, it is stored in a mixture containing inhibitors, namely diphenylamine in Grade A vinyl and hydroquinone in Grade H vinyl. Vinyl acetate is either polymerized alone or with vinyl chloride, acrylic esters, maleic acid and vinyl benzoate. These polymers are used as plastics, coatings and adhesives.

### Vinyl Chloride

Vinyl chloride is a colorless gas (BP -13.9°C) which is usually shipped and stored as a liquid under pressure. It is used in the production of polyvinyl chloride plastics.

The acute toxic effects of vinyl chloride monomer by inhalation are few and mild; at concentrations above 500 ppm it may slightly irritate the eyes. However, recent evidence suggests that very low concentrations of vinyl chloride inhaled over a period of time may cause liver pathology—most importantly, liver cancer.

The maximum permissible exposure level to vinyl chloride is not to exceed 1 ppm averaged over any 8-hour period, and no employee may be exposed to vinyl chloride concentrations greater than 5 ppm over any period of 15 minutes or less. The OSHA standard specifically excludes direct contact with liquid vinyl chloride.

### Noise

Noise or unwanted sound is classified as steady, intermittent, or impulsive depending on the type, rate and duration of the sound impulses. Noise exposures are typically found at blowers, pelletizers and comminuters in the plastics and resins industry.

The effect of noise on hearing depends on the level and spectrum of the noise, duration of exposure, the number of times it occurs per day, the number of years daily exposure is repeated and individual susceptibility. Excessive noise first induces auditory fatigue or temporary threshold shift. Normal hearing returns after a period of hours away from the noise source. Permanent threshold shift occurs after repeated exposures to excessive noise. This noise-induced hearing loss is a result of damage to the sensory hair cells in the organ of corti and the associated peripheral nerve fibers. Excessive noise can also cause extra-auditory effects, such as cardiovascular, neurologic, endocrine and biochemical changes.

The OSHA 8-hour TWA for non-impulsive noise is 90 dBA.



## GLOSSARY

ABSORPTION	The dissolution of one substance into another, such as a gas into a liquid.
ACGIH	American Conference of Governmental Industrial Hygienists.
ADSORPTION	The physical and chemical adherence of a gas to the surface of a solid.
AIR CHANGE	One replacement of air in a defined work area.
ANESTHETIC	The main toxic action is the depressant effect upon the central nervous system.
ATAXIA	Failure of muscle coordination.
AUTOCLAVE	A pressurized vessel capable of containing reacting fluids at high temperatures and pressures.
BELLOWS-TYPE SEAL	A seal as a transient between two unequal areas designed to allow lateral or vertical movement of one end of the seal without breaking the barrier.
BLEED VALVE	A small opening or valve in a totally enclosed pipe system or vessel that permits a flow of fluids at a rate sufficient to prevent undesirable accumulations of the fluids within the pipe system or vessel.
BLIND FLANGES	A flat surface usually made of metal, that is placed across a pipe flange to totally block the flow of fluids at that point in the pipe system.
BLOW-DOWN PROCEDURE	A sequence of steps involving the discharge of vessel or system contents and subsequently flushing or purging any residual quantities of the contents by means of another fluid.
CANOPY HOOD EXHAUST	A local overhead ventilation hood which is free-standing on at least three sides and draws air upwards into it.
CAPTURE VELOCITY	The air velocity at any point in front of an exhaust hood or exhaust opening necessary to overcome room air currents to draw the contaminated air at that point into the hood.
CEILING LIMIT	The air concentration which certain contaminants should not exceed.

CHARCOAL TUBES	Glass tubes which are filled with activated charcoal and used to collect air contaminants to determine their concentrations.
CHEMICAL CARTRIDGE RESPIRATOR	A breathing mask which isolates the breathing zone. The user breathes by drawing air through chemical cartridges which remove the contaminants by adsorption or reaction.
CONJUNCTIVITIS	Inflammation of the eye membranes.
CORYZA	Inflammation of the nasal mucous membranes with a profuse discharge from the nostrils.
CUTANEOUS ABSORPTION	Entrance to the body by going through the skin.
dba	The logarithmic range of sound pressure levels which approximates the ear's response characteristics.
DETECTOR TUBES	Tubes which give an approximate determination of specific air contaminants by the length of stain or degree of color change of the absorbent when a fixed volume of air is passed through it.
DISPERSION (EMULSION) POLYMERIZATION	Characterized by the location of the initiator in the aqueous phase and small size of resin particles.
DYSARTHRIA	The slurring of speech due to disturbances of muscular control which has resulted from damage to the nervous system.
EDEMA	Swelling.
ENGINEERING CONTROLS	The control of hazardous substances by modifying equipment, materials handling, production processes, work procedures, etc.
EXCURSION LEVELS	Concentration levels of specific contaminants which exceed the ceiling or Threshold Limit Values (TLV).
FUME SCRUBBER	A vessel equipped with water spray nozzles which removes particles and gases from the air stream passing through the water sprays.
GAS CHROMATOGRAPHY	The process in which the components of a mixture are separated from one another by volatilizing the sample into a carrier gas stream that is passed through a bed of packing material. Different chemicals move through the packing at different rates and are separated. The chemicals are identified by measuring changes in the properties of the gas stream.

GENERAL VENTILATION	A mechanical or natural method for exhausting large volumes of air from a large area, such as a room or entire building.
HEMOLYTIC ANEMIA	A reduction in the normal amount of red blood cells.
INERT GAS	A group of gases which will not react with other substances at the temperatures and pressures involved.
LACHRYMATION	Secretion and discharge of tears.
LOCAL EXHAUST	A ventilation system which exhausts air in local work zones located in a larger work area.
MAKE-UP AIR	Uncontaminated air that is used to replace air that has been exhausted.
NOISE DOSIMETRY	The technique of measuring the intensity and duration of noise exposures.
NUISANCE DUST	Airborne particulates which are not toxic, but due to high concentrations are hazardous.
PERSONAL PROTECTIVE EQUIPMENT	Devices which are worn by personnel to protect them from hazardous substances or physical agents.
PERSONAL SAMPLES	Samples of contaminants which are obtained from sampling devices worn by individuals.
REFLUX CONDENSER	A device which cools a vapor to its liquid phase and returns it to the reactor.
SOLENOID VALVE	A valve that is made either to close or open when an electrical current is passed through a coil surrounding a magnetic steel member attached to the valve stem.
SPECTACLE VALVE	An assembly consisting of pipe flanges that clamp a long flat plate with a hold on one end. When the pipe flange is loosened, the flat plate can be slid over manually to totally block the flow of fluids in the pipe. The flat plate has the physical appearance of a giant set of spectacles.
STRIPPING PROCESS	The process which separates unreacted materials from the reacted ones so that they may be conserved and employee exposure reduced when handling the reacted materials.

SUPPLIED AIR  
RESPIRATOR

A breathing device in which the breathing zone is isolated from the outside environment. Pure air is supplied to the breathing zone via an air line from either a tank worn by the individual or from a remote source.

TLV

Threshold Limit Value—These are guidelines for worker exposures to air contaminants and physical agents given in time-weighted average concentrations for a normal 8-hour workday or 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effects.

TWA

Time-Weighted Average—The average concentration of a component in air samples collected over the specified time interval.

VELOMETER

An instrument that measures air velocity and static pressure.

VERTIGO

Dizziness.

## REFERENCES

- American Conference of Governmental Industrial Hygienists. 1976. A manual of recommended practices, 14th ed. ACGIH, Lansing, Mich.
- Anderson, W. P. (Tenneco Chemical Company). 1975. Personal communication to Leslie B. Evans, Environmental Protection Agency, May 13, 1975.
- Arnstein, L. R. 1965. Pumping liquids effectively. *Paint Varn. Prod.* (Sept.):35-40.
- Baturin, V. V. 1972. *Fundamentals of industrial ventilation*, 3rd ed. Pergamon Press, Elmsford, N. Y.
- Bourne, L. B., and F. J. M. Milner. 1963. Polyester resin hazards. *Brit. J. Industr. Med.* 20:100-109.
- Boyle, John P., and Nicholas P. Novak. 1963. Predicting ventilation requirements for coating materials. *Ind. Hyg. J.* (Nov.-Dec.):606-610.
- Broughton, W. E. 1965. Epoxy resins in industry: The hazards and their control. *Ann. Occup. Hyg.* 8:131-142.
- Browning, R. L. 1969a. Analyzing industrial risks. *Chem. Eng.* (Oct. 20):114.
- Browning, R. L. 1969b. Calculating loss exposures. *Chem. Eng.* (Nov. 17):239.
- Browning, R. L. 1969c. Estimating loss probabilities. *Chem. Eng.* (Dec. 15):135-140.
- Burke, A. J. 1973. Weighing bulk materials in the process industries. *Chem. Eng.* (Mar. 5).
- Cattanach, J. B. 1974. Meeting noise objectives in the plastics industry. *Am. Ind. Hyg. Assoc. J.* 17:131-135.
- Chemical Engineering. 1974. A new unsaturated polyester cures or stops curing at the flip of a light switch. *Chem. Eng.* (Nov. 25):35.
- Chemical Engineering. 1975a. PVC makers move to mop up monomer emissions. *Chem. Eng.* (Nov. 24):25.
- Chemical Engineering. 1975b. A simple leak-detecting device for rupture disks. *Chem. Eng.* (Mar. 17):88.
- Chemical Engineering. 1975c. Unusually low concentrations of vinyl chloride in workplace ambient air. *Chem. Eng.* (Apr. 14):33.
- Chemical Week. 1976a. Getting out the last traces of VCM. *Chem. Week* (Aug. 11):35.
- Chemical Week. 1976b. Masked men get drop on VCM. *Chem. Week* (Apr. 7):32.
- Chemical Week. 1976c. Search spreads for SBR-cancer link. *Chem. Week* (May 12):58.
- Chemical Week. 1976d. Vinyl makers ready to clear air. *Chem. Week* (Jan. 28):33.
- Constance, John D. 1970. Estimating exhaust-air requirements for processes. *Chem. Eng.* (Aug. 10):116-118.
- Danielson, J. A., ed. 1973. *Air pollution engineering manual*. Environmental Protection Agency Publ. No. AP-40. EPA, Washington, D. C.
- DeGesero, R. A. 1974. The evaluation and control of chemicals in polystyrene manufacturing. *Ann. Occup. Hyg.* 17:123-129.

- Environmental Protection Agency. 1975a. Proceedings of Conference on Environmental Aspects of Chemical Use in Rubber Processing Operations Held in Akron, Ohio, Mar. 12-14, 1975. NTIS No. PB244172. EPA-560/1-75-002. Springfield, Va.
- Environmental Protection Agency. 1975b. Standard support and environmental impact statement: Emission standard for vinyl chloride. Publ. No. EPA-450/2-75-009. Air Pollution Technical Information Center, EPA, Research Triangle Park, N. C.
- Fitzpatrick, K. 1974. Polyethylene plant operations: Closure for high pressure piping systems. Chem. Eng. Prog. 70(9):60-61.
- Food Engineering. 1971. Fills powders, prevents dusts. Food Eng. (Aug.):83.
- Goldfield, Joseph, and Frederick E. Brandt. 1974. Dust control techniques in the asbestos industry. Am. Ind. Hyg. Assoc. J. 35(12):799-808.
- Goss, A. E., and A. M. Ross, Jr. 1953. Effective control of lead dust in the manufacture of vinyl plastics. Am. Ind. Hyg. Assoc. Q. 14(1):41-49.
- Hama, G. M. 1948. Ventilation for control of dust from bagging operations. Heat. Vent. (Apr.):91.
- Hemeon, W. C. L. 1963. Plant and process ventilation, 2nd ed. Industrial Press, Inc., New York, N. Y. 481 pp.
- Hile, H. B. 1974. Closing vents on compressor seals prevents loss of hydrocarbon gases. Chem. Eng. (Sept. 2):59.
- Hoy, F. F. 1974. Personal communication to Don R. Goodwin, Environmental Protection Agency. Firestone Plastics Company, Perryville, Md.
- Iammartino, N. R. 1975. PVC makers to mop up monomer emissions. Chem. Eng. (Nov. 24).
- Kingsley, W. H. 1958. Health hazards and control of an epoxy resin operation. Ind. Hyg. J. 19(3):258-260.
- Kleeberg, Charles F. (Environmental Protection Agency). 1974. Trip report: Tenneco, Burlington, N. J., plant inspection, Sept. 23, 1974.
- Kraus, M. N. 1969. Pneumatic conveyors. Chem. Eng. (Deskbook Issue: Oct. 13).
- Ludwig, E. G. 1973. Designing process plants to meet OSHA standards. Chem. Eng. (Sept.):88-100.
- Mack, W. A. 1975. VCM reduction and control. Chem. Eng. Prog. 71(9).
- Mallette, F. S. 1943. Industrial hygiene--in synthetic rubber manufacture. Ind. Med. 12(7):495-499.
- Mantell, G. J., J. T. Barr, and R. K. S. Chan. 1975. Stripping VCM from PVC resins. Chem. Eng. Prog. 7(9):54.
- McCormick, W. E. 1971. Environmental health control for the rubber industry. Rubber Chem. Technol. 44(2):512-533.
- Mudd, J. R. (Plant Manager, General Tire and Rubber Company, Ashtabula, Ohio). 1974. Personal communication to Don R. Goodwin, Environmental Protection Agency. June 17, 1974.
- National Institute for Occupational Safety and Health. 1976. Engineering control research recommendations. HEW Publ. No. (NIOSH) 76-180. U. S. Department of Health, Education and Welfare, Cincinnati, Ohio.
- Oelfke, K. J., Jr. (Manager, EDC and Derivatives, Dow Chemical, U.S.A.). 1974. Personal communication to Don R. Goodwin, Environmental Protection Agency, June 12, 1974.
- Oil and Gas Journal. 1976. Goodrich chloride levels below OSHA regulations. Oil Gas J. (Jan. 19):23.

- Osman, H. A., M. H. Wahdan, and M. H. Noweir. 1972. Health problems resulting from prolonged exposure to chemical agents in rubber industry. J. Egypt Public Health Assoc. 157:290-311.
- Owen, L. T. 1974. Selecting in-plant dust-control systems. Chem. Eng. (Oct. 14):120-126.
- Plastics World. 1976. PVC, VCM plants operate within OSHA regulations. Plastics World (Jan. 19):7.
- Rothman, Robert A. 1973. Gaskets and packings. Chem. Eng. (Feb. 26):69-74.
- Rowe, V. K. 1975. Experience in industrial exposure control. Ann. N. Y. Acad. Sci. 246:306-310.
- Russell, W. W. 1974. Loss prevention: Safety in flange joints. Chem. Eng. Prog. 70(4):68-72.
- Sargent, Edward F., Charles A. Mitchell, and Robert E. Brubaker. 1976. Respiratory effects of occupational exposure to an epoxy resin system. Arch. Environ. Health (Sept.-Oct.):236-240.
- Schoenberg, Janet B., and Charles A. Mitchell. 1975. Airway disease caused by phenolic (phenol-formaldehyde) resin exposure. Arch. Environ. Health 30 (Dec.):574.
- Stern, A. C., and L. D. Horowitz. 1953. Industrial hygiene in the paint factory. N. Y. State Department of Labor Monthly Rev. 32:2.
- Templeton, Harold C. 1971. Valve installation, operation and maintenance. Chem. Eng. (Oct. 11):141-149.
- Uncles, R. F. 1969. Containers and packaging. Chem. Eng. (Deskbook Issue):Oct. 13).
- Van Ingen, R. E. (Manager, Manufacturing Environmental Conversion Department, Shell Oil Company). 1974. Personal communication to Don R. Goodwin, Environmental Protection Agency, Dec. 6, 1974.
- Wheeler, R. N., and M. E. Sutherland. 1975. Control of in-transit VCM. Chem. Eng. Prog. 71(9):48-53.
- Wiley, Samuel K. 1973. Controlling vapor losses. Chem. Eng. (Sept. 17):116-119.